

## The Isolation and Identification of an Unusual Palladium(II) Substituted *Dien* Complex [1]

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In the course of undertaking detailed kinetic studies of fast substitution reactions of a series of palladium(II) substituted *dien* complexes [2], we tried to simplify the preparation procedure given in the literature [3] for the complex species Pd( $\text{Me}_3\text{dien}$ )X<sup>+</sup> ( $\text{Me}_3\text{dien}$  = 1,4,7-trimethyldiethylenetriamine). In this method LiBr is added to the reaction solution containing PdCl<sub>4</sub><sup>2-</sup>,  $\text{Me}_3\text{dien}$  and HCl, and the orange oil formed on addition of ethanol and ether to the volume reduced solution is left for twelve days in a refrigerator. In the present work we isolated our product from an identical reaction solution, but without the addition of a precipitating salt. Since an excess of chloride ion was already available in solution to form the chloro (*i.e.* X = Cl) species, the addition of an alternative precipitating salt was not desirable. Moreover, possible contamination of the precipitated product could thereby be prevented. The isolation proceeded effortlessly, but the product turned out to be a somewhat unusual complex Pd( $\text{Me}_3\text{dien}$ )Cl<sub>2</sub>·HCl, rather than the complex [Pd( $\text{Me}_3\text{dien}$ )Cl]Cl which we had expected: nevertheless it yields in aqueous solution the desired species Pd( $\text{Me}_3\text{dien}$ )Cl<sup>+</sup>, making it worthwhile to report its synthesis and identification.

### Experimental

#### Synthesis

A mixture of 1 g of PdCl<sub>2</sub>, 3 cm<sup>3</sup> of concentrated HCl and 17 cm<sup>3</sup> of H<sub>2</sub>O was stirred magnetically until a deep red solution indicating dissolution of the PdCl<sub>2</sub> was obtained. The amine<sup>‡</sup> was added dropwise to the stirred solution until the original deep red colour changed to yellow (*ca.* 2–3 cm<sup>3</sup>). The solution was filtered and the filtrate (pH *ca.* 2) was evaporated

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<sup>‡</sup> $\text{Me}_3\text{dien}$  supplied by Aldrich Chemical Company and analysed in our Institute using NMR spectroscopy.

until an orange oil remained. This was dissolved in 25 cm<sup>3</sup> of ethanol and the yellow product separated on stirring: this was recrystallized from a highly concentrated aqueous solution by the addition of ethanol, and was finally washed with ice-cold ethanol and diethylether.

#### Identification

The isolated product was chemically analysed for C, H, N and Cl<sup>§</sup>. The pH titration of an aqueous solution of the complex was performed with a Metrohm E520 pH meter and an extended-scale burette filled with Merck Titrisol alkali solution. The removal of free chloride ion from aqueous solutions of the complex was accomplished with Merck Lewatit M5080 G3 anion exchanger converted into the perchlorate form. A Perkin Elmer 555 UV/visible spectrophotometer was employed for the spectral identification of the complex species present in prepared aqueous solutions, in eluates obtained by passing aqueous solutions through the anion exchanger and in filtrates of aqueous solutions treated with AgClO<sub>4</sub> to convert chloro species into aquo species by precipitation of chloride as AgCl. The preliminary kinetic results for a substitution reaction of the complex in aqueous solution were obtained with an Aminco stopped-flow apparatus.

### Results and Discussion

A comparison between the results of the chemical analysis of the isolated product (%C = 23.5; %H = 5.5; %N = 11.8; %Cl = 29.3) and the corresponding values calculated for the complexes [Pd( $\text{Me}_3\text{dien}$ )Cl]Cl (%C = 26.1; %H = 5.9; %N = 13.0; %Cl = 22.0) and Pd( $\text{Me}_3\text{dien}$ )Cl<sub>2</sub>·HCl (%C = 23.4; %H = 5.6; %N = 11.7; %Cl = 29.6) leaves no doubt about the identity of the product. Its structure, however, remains uncertain. The reason for this is that the complex is isolated as a powder and not as a crystalline substance, making it unsuitable for structural analysis. We have not yet succeeded in growing crystals for this purpose. The complex can either be a monochloro species with one mol HCl of crystallization, *viz.* [Pd( $\text{Me}_3\text{dien}$ )Cl]Cl·HCl, or a dichloro species with HCl attached to the third, uncoordinated site of the *dien* ligand, *viz.* [Pd( $\text{Me}_3\text{dien}$ )Cl<sub>2</sub>]HCl. The non-crystalline nature of the isolated complex and its inability to lose HCl of crystallization on heating at 110 °C as in the case of, for instance, the complex *trans*-[Co(en)<sub>2</sub>Cl<sub>2</sub>]Cl·HCl [4, 5], make the former possibility less probable. We have made a number of

<sup>§</sup> C, H, N and Cl analyses performed by Hoechst Analytical Laboratory, Frankfurt/Main.

observations in favour of the assigned chemical formula and the existence of the complex as a dichloro species in the solid state and these are described below.

It is assumed that on dissolution into water each complex molecule  $[\text{Pd}(\text{Me}_3\text{dien})\text{Cl}_2]\text{HCl}$  releases HCl and undergoes ring-closure with the release of one coordinated chloride ligand to yield the species  $\text{Pd}(\text{Me}_3\text{dien})\text{Cl}^+$ . The complex has a much higher rate of dissolution into water than any other palladium(II) substituted *dien* complex and this could be due to the ease of ring-closure in water, a process most likely prevented in the preparation solution with its high [HCl]. The presence of the ring-closed species  $\text{Pd}(\text{Me}_3\text{dien})\text{Cl}^+$  in aqueous solution is confirmed by the satisfactory agreement between measured ( $\lambda_{\text{max}} = 339 \text{ nm}$ ,  $\epsilon_{\text{max}} = 671 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ ) and reported ( $\lambda_{\text{max}} = 342 \text{ nm}$ ,  $\epsilon_{\text{max}} = 635 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ ) spectral data [3]. The higher dissolution rate can also be accounted for by the fact that the complex was isolated as a chloride salt in powder form whereas all the other complexes which we studied [2] were isolated as crystalline perchlorates.

The release of one hydrogen ion by each complex molecule on dissolution into water was one of our first observations. The initial pH of an aqueous solution of the complex is, unlike all the other palladium(II) substituted *dien* complexes yielding almost neutral aqueous solutions [2], directly related to its concentration (e.g. pH = 3 for  $[\text{Pd}] = 1 \times 10^{-3} \text{ mol dm}^{-3}$ ). The pH titration curve in Fig. 1 shows that the free hydrogen ion per complex molecule can be neutralized by the addition of an amount of alkali equivalent to the [Pd] in solution, leading to a pH value comparable with those of all other substituted *dien* complexes of palladium(II) in the chloride form. In addition, no spectral changes were observed during this neutralization process, indicating that only free hydrogen ions were titrated. Further addition of

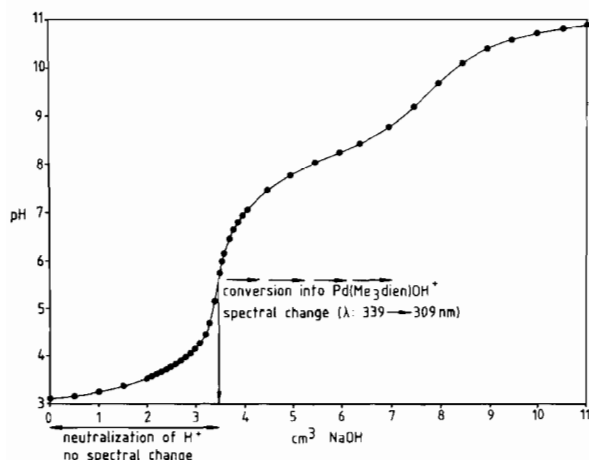


Fig. 1. pH titration of  $\text{Pd}(\text{Me}_3\text{dien})\text{Cl}^+$ ;  $[\text{Pd}] = 7.2 \times 10^{-4} \text{ mol dm}^{-3}$  (50  $\text{cm}^3$ );  $[\text{NaOH}] = 0.01 \text{ mol dm}^{-3}$ .

alkali, however, resulted in significant spectral changes due to the formation of  $\text{Pd}(\text{Me}_3\text{dien})\text{OH}^+$ .

The presence of two free chloride ions per complex ion in aqueous solution was proven by passing a solution of a given concentration through the anion exchanger described above, treating the eluate with one equivalent of  $\text{AgClO}_4$  to convert the complex species into the aquo form and comparing the UV/visible spectrum of the filtrate with that of a second, identical solution of the complex not passed through the exchange column but treated with three equivalents of  $\text{AgClO}_4$  to convert the chloro species into an aquo species. The spectral data ( $\lambda_{\text{max}} = 322/321 \text{ nm}$ ,  $\epsilon_{\text{max}} = 818/862 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ ) were identical within 5%, slight deviations being acceptable in view of the effectiveness of chloride removal by the anion exchanger and/or the accuracy of recovering all of the complex solution from the exchange column.

The complex  $[\text{Pd}(\text{Me}_3\text{dien})\text{Cl}]\text{Cl}$  which we initially thought to have isolated, would in aqueous solution require treatment with two equivalents of  $\text{AgClO}_4$  to convert it into the corresponding aquo species  $\text{Pd}(\text{Me}_3\text{dien})\text{OH}_2^+$ . However, treatment of an aqueous solution of the isolated complex with two equivalents of  $\text{AgClO}_4$  led for a substitution reaction by iodide to the acquisition of kinetic data that are identical to those obtained for a corresponding aqueous solution of the complex itself, instead of being in agreement with the anation data expected for palladium(II) substituted *dien* complexes. This is illustrated by the entries in Table I, representing some preliminary kinetic measurements for the above-mentioned substitution reaction and involving aqueous solutions of the complex treated with zero, two and three equivalents of  $\text{AgClO}_4$ . The results for the first two cases are, within experimental error limits, identical. This can be explained in terms of the precipitation (as AgCl) of the two free chloride ions per complex molecule in the second case without conversion of the available chloro complex species into the corresponding aquo species. In the third case the aquo species is indeed available. Its anation reaction by iodide is so fast that it could not be measured under the stated conditions with the available stopped-flow equipment. This is in agreement with what is expected for a less sterically hindered *dien* complex in view of, for instance, the anation of  $\text{Pd}(\text{dien})\text{OH}_2^+$  by  $\text{Cl}^-$  [4] that occurs within the mixing time of the stopped-flow instrument.

A further proof for the existence of the isolated product in the solid state as a dichloro complex might be furnished by our inability to isolate the corresponding perchlorate species, since in the preparation of other palladium(II) substituted *dien* complexes the perchlorate salts of monochloro complexes could easily be isolated [2, 3]. The attachment of HCl to one of the three coordination sites of the *dien* ligand

TABLE I. Preliminary Kinetic Measurements for Iodide Substitution involving Complex Solutions Treated with Various Amounts of AgClO<sub>4</sub>. [Pd] = 1 × 10<sup>-3</sup> mol dm<sup>-3</sup>; ionic strength = 0.1 mol dm<sup>-3</sup>, wavelength = 390 nm.

Solution	[I <sup>-</sup> ]/mol dm <sup>-3</sup>	k <sub>obs</sub> /s <sup>-1</sup>	
		11.5 °C	25.0 °C
aqueous solution of isolated product <i>not</i> treated with AgClO <sub>4</sub>	5 × 10 <sup>-3</sup>	24.2 ± 0.5	40.9 ± 1.0
	1 × 10 <sup>-2</sup>	36.5 ± 0.4	63.2 ± 0.8
	2 × 10 <sup>-2</sup>	58.9 ± 0.5	94.9 ± 3.4
	3 × 10 <sup>-2</sup>	87.0 ± 0.6	
		k <sub>1</sub> /s <sup>-1</sup> : k <sub>2</sub> /dm <sup>3</sup> mol <sup>-1</sup> s <sup>-1</sup> :	11.3 ± 1.7 2486 ± 91
aqueous solution of isolated product treated with <i>two</i> equivalents of AgClO <sub>4</sub>	5 × 10 <sup>-3</sup>		
	1 × 10 <sup>-2</sup>	36.5 ± 0.8	41.6 ± 0.8
	2 × 10 <sup>-2</sup>	64.7 ± 1.3	61.3 ± 0.8
	3 × 10 <sup>-2</sup>	91.5 ± 0.3	103 ± 3
		k <sub>1</sub> /s <sup>-1</sup> : k <sub>2</sub> /dm <sup>3</sup> mol <sup>-1</sup> s <sup>-1</sup> :	9.16 ± 0.94 2754 ± 43
aqueous solution of isolated product treated with <i>three</i> equivalents of AgClO <sub>4</sub>	5 × 10 <sup>-3</sup>	not measurable	
	1 × 10 <sup>-2</sup>	with available	
	2 × 10 <sup>-2</sup>	stopped-flow	
	3 × 10 <sup>-2</sup>	equipment	

will cause two chloride ions to remain in the coordination sphere during the reaction of the ligand with PdCl<sub>4</sub><sup>2-</sup>, resulting in a neutral complex that can only be isolated by evaporation of the reaction solution and not by addition of perchlorate to yield a perchlorate complex species.

In summary we isolated in an extremely easy and direct manner a complex which we thought was [Pd(Me<sub>3</sub>dien)Cl]Cl. Numerous evidence was found that it is instead most probably the complex [Pd-(Me<sub>3</sub>dien)Cl<sub>2</sub>]HCl. It yields in aqueous solution the species Pd(Me<sub>3</sub>dien)Cl<sup>+</sup> and, by treatment with three equivalents of AgClO<sub>4</sub>, the species Pd(Me<sub>3</sub>dien)OH<sub>2</sub><sup>2+</sup>, both needed for kinetic studies concerning fast substitution reactions [2].

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