

THERMAL DECOMPOSITION OF SOME IMIDAZOLE AND N-METHYL SUBSTITUTED IMIDAZOLE COMPLEXES OF PALLADIUM(II)

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We describe in this paper the thermal decomposition in air of several complexes of palladium(II) chloride with imidazole and N-methylimidazole. Although the final process of the decomposition gives $(PdCl_2)_n$ which then decomposes to palladium which oxidizes to PdO, there are interesting differences in the initial decomposition path. The reasons for these differences appear to be related to the trans-effect and to the presence in the imidazole complexes of hydrogen bonds which break down at temperatures of around 220°.

This paper is the first of a series dedicated to the study of several complexes of palladium(II) chloride with imidazole and N-substituted imidazole. We describe here the thermal decomposition of some of these complexes in air. No attempt was made to obtain kinetic data, our main interest being to determine the existence of new species formed during the process of decomposition. Although the thermal decomposition of palladium complexes is a fertile area of study [1], there are, to our knowledge, no previous reports of the thermal behaviour of palladium imidazole complexes. The only example referring to complexes of this kind with elements of the nickel group refer to nickel(II) complexes [2] which, as expected from the general trends in the chemistry of nickel, palladium and platinum [3], differ considerably from those studied here.

Experimental

All the complexes were obtained as described in reference [7].

The thermoanalytical curves were obtained on a Mettler 181 thermoanalyser. Samples of ~ 10 mg were placed on uncovered platinum crucibles located on top of the thermocouple. The heating rate was standardized at 10°/min. The runs were performed on still air. For the DTA, the sensitivity was fixed at 100 μ V for full scale deflection while for the DTG it was 1 mg/min.

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Results and discussion

The thermoanalytical curves (DTA, TG and DTG) of the several compounds studied are given in Figs 1 to 6. It can be seen that the complete process of decomposition in air, in the range of temperatures employed, 25–900°, includes several thermal effects in all cases.

In Fig. 1 the curves corresponding to $[\text{Pd}(\text{ImH})_4]\text{Cl}_2$ are given. It is clear that there are five endothermic peaks with their maxima at the temperatures of ~ 280, 310, 380, 450 and 890°. There is also a very marked exothermic effect with its maximum at 580° and a kind of shoulder centred at ~ 510°.

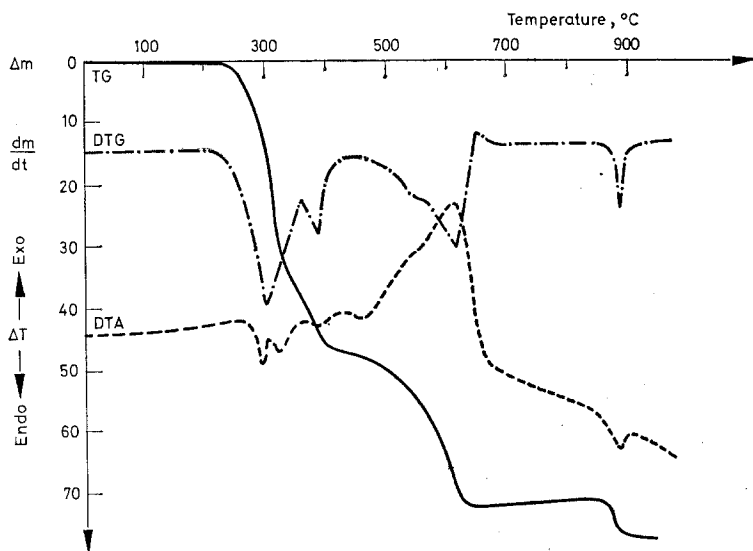
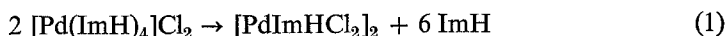


Fig. 1. Thermoanalytical curves for $[\text{Pd}(\text{ImH})_4]\text{Cl}_2$ in air

From the TG plot it appears that the decomposition starts at about 250° and although there are no clear steps in this curve, the information contained on the DTG curve can help in deciding the stoichiometry of the processes occurring. It seems then that under this dynamic condition the maximum decomposition rate is attained at near 300°, however, before this process of decomposition ends another increase on the rate of weight loss is observed and it is accompanied by a small endotherm on the DTA curve. Both these peaks have their maxima at ~ 380°. The weight loss recorded up to the end of these peaks, at 425°, is 45.39% and can be fitted to the following reaction:

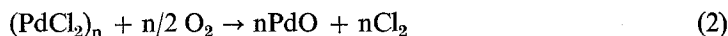


for which the calculated weight loss is 45.69%. If this stoichiometry is correct, and taking into account the marked tendency of palladium to form multinuclear

halogen bridged complexes [4] we could assume that the product of the thermal decomposition in air of $[\text{Pd}(\text{ImH})_4]\text{Cl}_2$ is either cis or trans dichloro- μ -dichloro-diimidazole dipalladium(II).

At first sight it appears that this behaviour is different from that shown by the palladium tetraamine complexes $[\text{Pd}(\text{NH}_3)_4]\text{Cl}_2$ which, according to Wendlandt and Funes [5], evolve initially two moles of ammonia giving the dichlorodiamino complexes $[\text{Pd}(\text{NH}_3)_2\text{Cl}_2]$. However, since the DTG curve shows two clearly different peaks, centred at 310° and 380° , it could be that the first one, for which the weight loss is comparatively greater, will correspond effectively to the elimination of two imidazole molecules for every palladium atom giving dichlorodiimidazole palladium(II). The second process, where the weight loss is smaller, would then be responsible of the elimination of another imidazole molecule for each palladium atom. This last process will then produce the dimer indicated above.

At higher temperatures there is another loss of weight, also reflected by an endotherm (peak at $\sim 450^\circ$), which is followed by two exotherms. The first of these processes could be due to the elimination of the last imidazole molecule, a reaction which should be endothermic, and the concomitant formation of $(\text{PdCl}_2)_n$, which is known to be stable up to this temperature. However this process cannot be clearly differentiated from the oxidation of the palladium halide:



which will be responsible of the very marked exotherm centred at 580° . There are two more interesting aspects on this process: one is that, according to Eq. (2), there should be a net weight loss of 30.92%, while it can be observed that, after 630° there is a weight gain on the TG curve this seems to be an indication that the

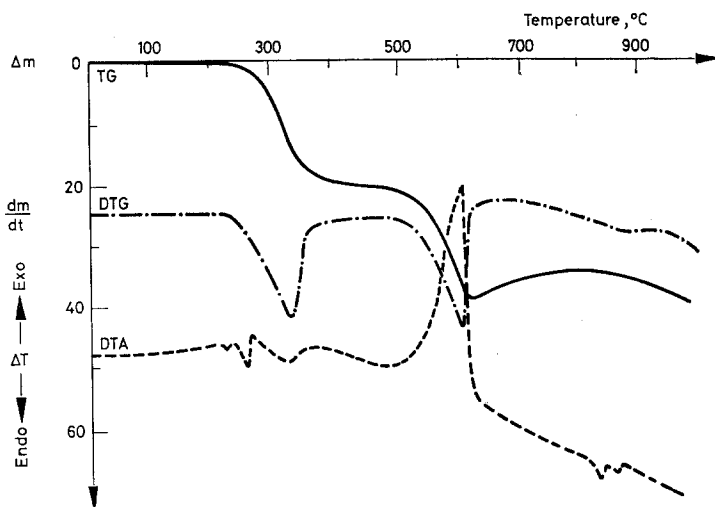


Fig. 2. Thermoanalytical curves for cis- $[\text{Pd}(\text{ImH})_2\text{Cl}_2] \cdot 2\text{KCl}$ in air

$(\text{PdCl}_2)_n$ is totally decomposed before the resulting palladium metal is completely oxidized. The weight gain in this oxidation will then be responsible of the slight mass increase up to $\sim 850^\circ$.

The second interesting point is the shoulder which appears on the main exothermic peak at about 550° . Although a kinetic study of the decomposition will be needed before a full explanation can be given, it could be due to the oxidation of some imidazole retained by the halide.

At temperatures over 850° , the palladium monoxide previously formed decomposes to the metal according to



for which the weight loss calculated (17.06%) is in fair accord with the experimental value of 15.03%.

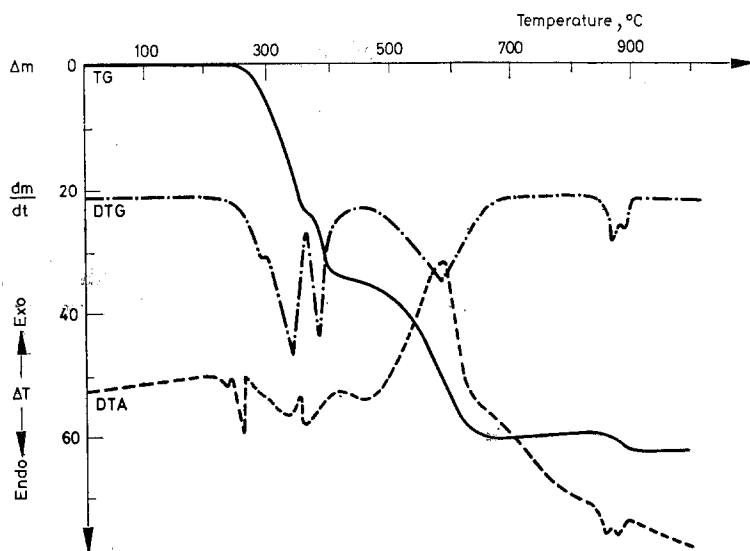


Fig. 3. Thermoanalytical curves for $\text{trans-[Pd(ImH)}_2\text{Cl}_2]$ in air

The thermoanalytical curves of $[\text{Pd(ImH)}_4]\text{Cl}_2 \cdot 2\text{KCl}$ were analogous to those first discussed for $[\text{Pd(ImH)}_4]\text{Cl}_2$. The only difference noted being a slight change on the shape of the 580° exotherm. On the other hand, both species gave identical IR spectra up to 150 cm^{-1} , below which value the lattice vibrations of both crystals are expected. This is a strong indication that the palladium(II) complex is the same in both cases and that the KCl is present as such in a kind of two-phase mixture. In it, the potassium halide affects slightly the elimination of the last imidazole molecule.

The thermoanalytical curves corresponding to the next two complexes studied: $\text{cis-[Pd(ImH}_2\text{Cl}_2)] \cdot 2\text{KCl}$ and $\text{trans-[Pd(ImH)}_2\text{Cl}_2]$ are given in Figs 2 and 3 re-

spectively. It can be appreciated that the curves are identical after 450°. At lower temperatures, however, there are only three thermal effects in the cis-complex while there are four on the trans-complex. Nevertheless, in both cases a small endothermic effect appears with its maximum at 220° before the TG curve shows any sign of decomposition; then, there is a marked and sharp endotherm centred at 257°. Both these peaks were reversible and only a very small hysteresis was observed for them. With regard to the first one there are two likely explanations: breaking of hydrogen bonds, which could be expected to form between the hydrogen bonded to the nitrogen atom in the imidazole ligand of a complex and a chlorine atom

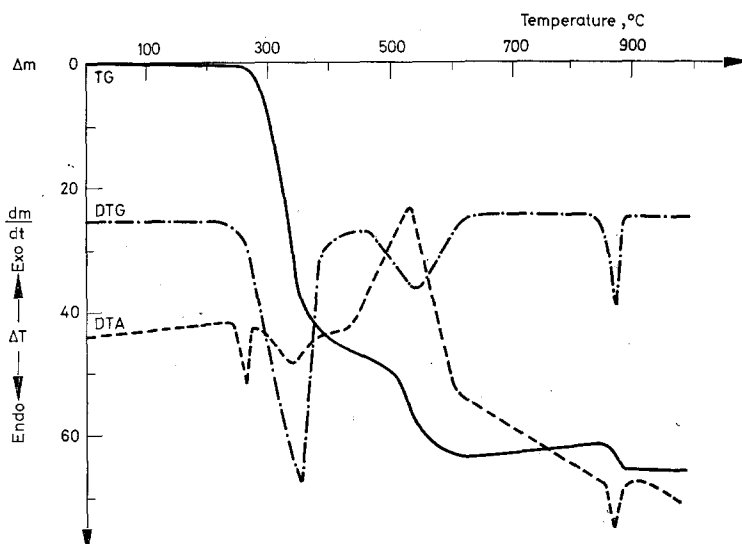
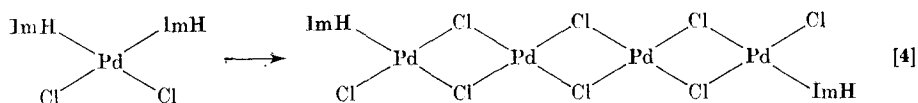


Fig. 4. Thermoanalytical curves for cis-[Pd(N-MIm)₂Cl₂] in air

in the imidazole ligand of a complex and a chlorine atom of a next-neighbour complex. The other explanation could be a phase transition since, for example, in the case of the analogous trans-[Pd(NH₃)₂Cl₂] there are two crystal modifications: low temperature monoclinic and high temperature tetragonal [6]. However, since this small first peak does not appear on the DTA curves of the cis and trans isomers of the N-methylimidazole analogues, Figs 4 and 5, we believe that the first explanation is more likely. Moreover, the existence of hydrogen bonds is confirmed by the presence, in the infrared spectra of the imidazole complexes [7] of bands at 3300 and 2800 cm⁻¹ which can be attributed to the νN-H stretching vibration and also at 1170 and 710 cm⁻¹ which can be attributed to the deformation modes δCNH within the molecular plane and γCNH out of the plane respectively, that can be assimilated to hydrogen bonding analogous to that operating in solid imidazole [8].

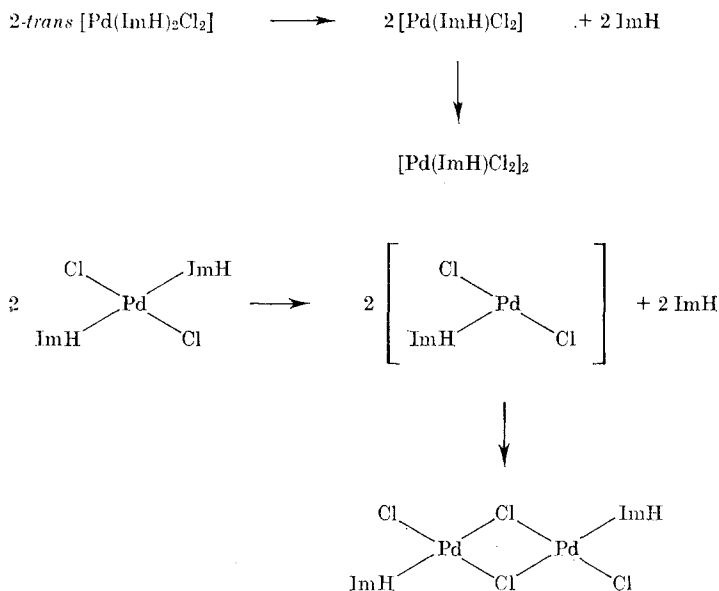
The second endothermic peak can be attributed to the melting and the simultaneous commencement of the decomposition.

In the case of the cis-complex, Fig. 2, according to the TG and DTG curves the first decomposition step seems to end near 480° and the weight loss recorded is equivalent to the loss of three imidazole molecules for each palladium atom. This probably means the formation of a chlorine bridged tetramer: these kind of tetramers are not uncommon in palladium chemistry [4]. It is also worth mentioning that there is only one peak in each of the DTA and DTG curves suggesting that the decomposition happens in one only step.



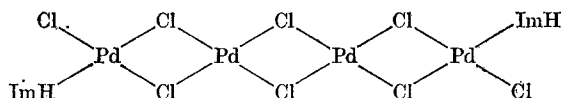
However, in the trans-complex, Fig. 3, there are two endothermic effects at 310 and 360° on the DTA plot and also two clear steps in the TG curve, also reflected on the DTG plot by two peaks. The amount decomposed on the first process is equivalent to a molecule of imidazole for every palladium atom, while the second corresponds to one imidazole molecule for two palladium atoms.

Under these conditions, one can postulate that the first step happens according to the following scheme [5,6] in which an unstable three coordinated intermediate



complex is formed. The association of two of those intermediates will then always give a trans dimer. In the second step, a tetramer is formed in which the palladium

atoms are chlorine bridged and the two imidazole molecules are again trans to each other:



This different behaviour of the cis and trans-dichloro-diimidazole palladium(II) can be attributed to the different trans influence of the chlorine ligands in both complexes. That is, in the case of the cis-complex, both chlorine ligands produce

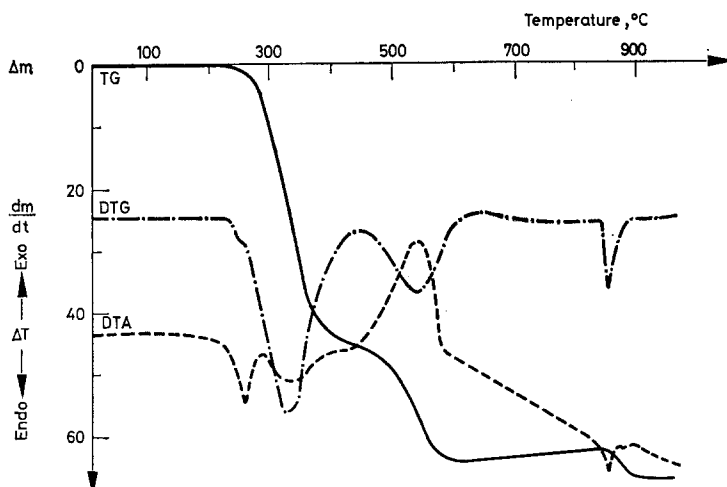


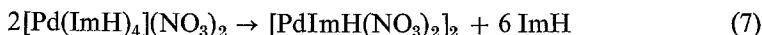
Fig. 5. Thermoanalytical curves for trans-[Pd(N-MIm)₂Cl₂] in air

the same trans influence and presumably, although not necessarily [9], the trans effect. However, in the case of the trans-complex the chlorine ligands are trans to each other and the formation of the tetramer happens in two steps.

The tetramer so formed decomposes to (PdCl₂)_n which then gives the metal and this is further oxidized to PdO as in the case of [Pd(ImH)₄]Cl₂ discussed above.

The thermal behaviour of cis and trans dichloro-di-N-methylimidazole palladium (II) seems somewhat simpler and moreover, both these complexes behave similarly, Figs 4 and 5. Apart from the absence of hydrogen bonds, the decomposition seems to start after the melting point, which in both cases is close to 280°. On the other hand, the elimination of all the N-methylimidazole occurs in one only step, clearly reflected on the TG curves (weight loss calculated 48.08%; experimental cis-complex 46.37%, trans-complex 45.0%), and also by an endotherm centred at ~ 350° on both the DTA curves. The palladium chloride formed then decomposes as indicated above. Once more, the presence of KCl in the cis-complex does not seem to disturb the thermal behaviour in any marked way.

In the case of the nitrate of tetraimidazole palladium(II), Fig. 6, the thermal decomposition in air starts at 190°. The first step of the decomposition is clearly delineated on the TG curve from which an experimental weight loss of 40.59% is obtained. This is equivalent to the evolution of three imidazole molecules for every palladium atom. Now, for the process



in which two nitrate groups move from the outer to the inner coordination sphere of the metal, the calculated weight loss is 42%, and a doubly nitrate-bridged dimer is formed. This process should be exothermic and is similar to those found in the cases of several complexes of Co(II), Co(III) [10, 11], Cr(III) [12], Pt(II) and Pt(IV) [13] having ammonia in the coordination sphere and nitrate ions in the ionization sphere. It is not clear however if the dimer complex is cis- or trans-. A second step, also very markedly exothermic, seems to be due to the elimination of

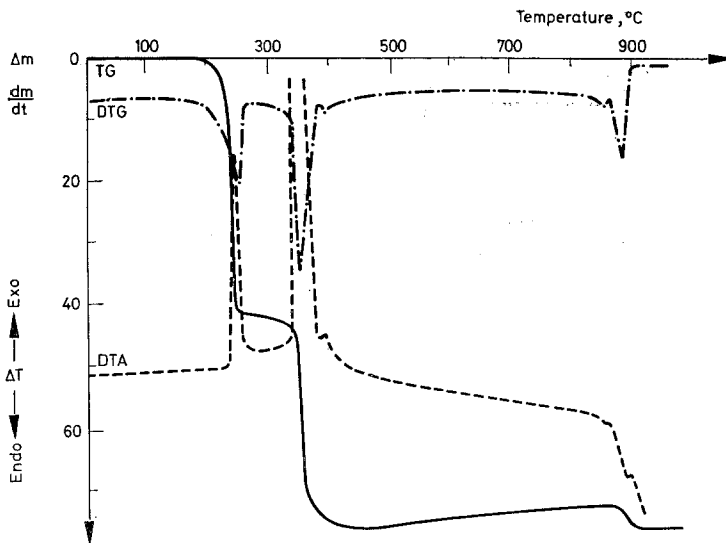
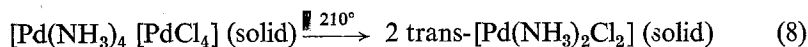


Fig. 6. Thermoanalytical curves for $[\text{Pd}(\text{ImH})_4](\text{NO}_3)_2$ in air

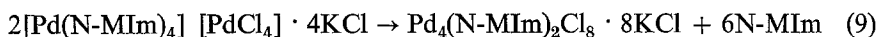
the remaining imidazole the decomposition of the nitrate and the oxidation of the palladium so formed. Nevertheless this process seems to happen in a relatively small temperature range — 325 to 420° — and afterwards some free palladium still remaining is converted to PdO, which decomposes to the metal at higher temperatures. It is interesting to note that the decomposition of PdO happens sometimes in one step and sometimes in two steps, so it appears that the Pd-O system is worth of further study.

We have also studied the thermal decomposition in air of a Magnus' Green salt analogue, $[\text{Pd}(\text{N-MIm})_4][\text{PdCl}_4] \cdot 4\text{KCl}$. It is noteworthy that the decomposition temperature is ~ 270°, some 60° over that of the ammine complex $[\text{Pd}(\text{NH}_3)_4]$

$[\text{PdCl}_4]$ [14]. On the other hand, we did not find any exotherm near 210° , characteristic of the isomerization of this kind of complex [15], like:



This can perhaps be due to bulkier size of the N-methylimidazole molecule which will then experience higher diffusion barriers. On the other hand, the first horizontal step in the TG plot seemed to correspond to the process:



for which the calculated weight loss is 25.08% while the experimental one is 27.03%. It seems then that here also one can obtain a chlorine-bridged tetramer with two terminal, probably trans, positions held by the two N-methylimidazole ligands. Subsequently the tetramer decomposes according to the usual pattern.

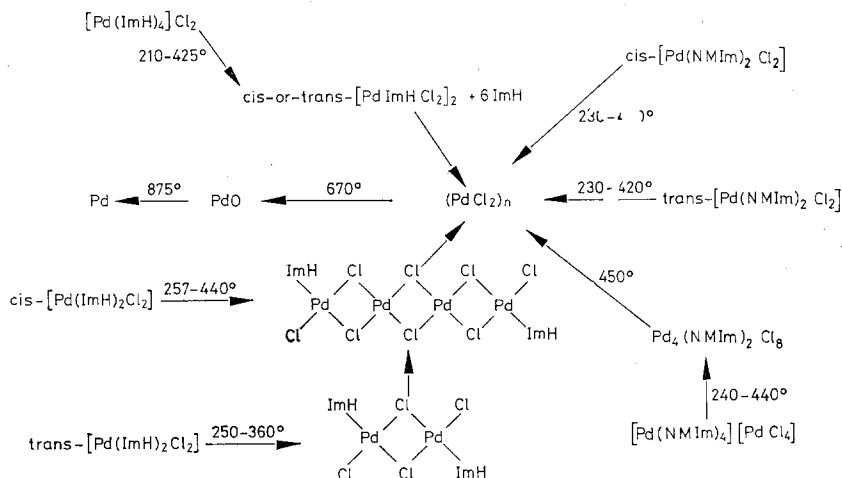


Fig. 7. Scheme of the thermal decomposition of some imidazole palladium(II) complexes in still air. ImH = Imidazole; N-MIm = N-methylimidazole

The thermal decomposition of all the complexes studied in this work, with the exception of the nitrate of tetraimidazole palladium(II), can be summarized, as in Fig. 7. It can be concluded that, although ultimately all these complexes give $(\text{PdCl}_2)_n$, which in its turn decomposes to Pd and oxidizes to PdO, there are marked differences in their behaviour. Of particular note are the absence of dimers and tetramers in the case of N-methyl-substituted imidazole complexes which both decompose directly to $(\text{PdCl}_2)_n$.

Perhaps the more interesting result is the different behaviour of the cis- and trans-dichloro diimidazole palladium(II) complexes where, probably due to the different trans effect, one can obtain a tetramer and a dimer and subsequently a tetramer before the formation of $(\text{PdCl}_2)_n$.

A somewhat conflicting point is that the dimer formed in the thermal decomposition of the dichloride of tetraimidazole palladium(II) does decompose to $(\text{PdCl}_2)_n$

at $\sim 425^\circ$, while the trans-dimer of the same empirical formulae $[\text{Pd}(\text{ImH})\text{Cl}_2]_2$ originated from trans-dichloro diimidazole palladium(II) forms a tetramer in the range $360\text{--}450^\circ$. Although this could be due to the first dimer being a cis-one, their decomposition being then different because of a different trans effect, this is a somewhat tenuous argument and we plan to investigate it further in future work.

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RÉSUMÉ — La décomposition thermique dans l'air de plusieurs complexes du chlorure de palladium(II) avec l'imidazole et le méthyl-4-imidazole est décrite. Bien que l'étape finale de la décomposition donne $(\text{PdCl}_2)_n$ qui se décompose ensuite en palladium qui s'oxyde en PdO, des différences intéressantes apparaissent dans les étapes initiales de la décomposition. Les causes de ces différences sont en rapport avec l'effet trans et la présence, dans les complexes avec l'imidazole, de liaisons hydrogène qui se rompent vers 220° .

ZUSAMMENFASSUNG — In diesem Beitrag wird die thermische Zersetzung verschiedener Komplexe des Palladium(II)chlorids mit Imidazol und N-Methylimidazol in Luft beschrieben. Obwohl der Endvorgang der Zersetzung $(\text{PdCl}_2)_n$ ergibt, welches dann zu Palladium zersetzt und zu PdO oxidiert wird, bestehen interessante Unterschiede im Anfangsschritt der Zersetzung. Die Ursachen dieser Unterschiede scheinen mit dem Trans-Effekt und der Anwesenheit von Wasserstoffbindungen in den Imidazolkomplexen verbunden zu sein, welche bei Temperaturen um 220° zerstört werden.

Резюме — Описано термическое разложение в воздушной атмосфере нескольких комплексов хлористого палладия(II) с имидазолом и И-метилимидазолом. Хотя конечный процесс разложения приводит к соединению $(\text{PdCl}_2)_n$, которое затем разлагается до палладия, окисляющегося до PdO, наблюдали интересные различия в начальной стадии разложения. Очевидно, что причины этих различий связаны с транс-эффектом и наличием в имидазольных комплексах водородных связей, которые разрываются при температуре около 220° .