Simple Preparation of Palladium(II) Complexes and Determination of Their Structures by Infrared Spectroscopy

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Square-planar complexes of palladium(II) and platinum(II) are among the most typical 16-electron coordination compounds (1). The addition of ligands to metal halides such as PdCl₂ and PtCl₂ is one of the most usual ways of preparing these complexes (1). In this paper we propose a series of simple and inexpensive experiments that allow the synthesis of several square-planar palladium(II) complexes and their study by infrared spectroscopy. As a suitable ligand for this purpose we have chosen the 2-benzoylpyridine, NC₆H₄- CO–C₆H₅ (bopy, see Scheme I), because of its very informative infrared spectrum, especially the absorption corresponding to the stretching v(CO) of the ketonic fragment.

In a recent paper we described the syntheses and structural characterization of several pentafluorophenyl complexes of palladium(II) and platinum(II) containing the bopy ligand (2). We have found that bopy has the ability to act as a denticulate chelate ligand by using the pyridine nitrogen and ketonic oxygen atoms as donor centers. Nevertheless, the M−O bond is much weaker than the M−N one, the first being easily broken by the addition of neutral or anionic ligands such as phosphines, carbon monoxide, or halides. One clearly noticeable feature in the infrared spectra of all these complexes is the variation of the frequency of the absorption v(CO) appearing at lower values in the chelating situation (ca. 130 cm⁻¹) than when the oxygen atom is not bonded to the metal center. Thus v(CO) is 1558 cm⁻¹ for [Pt(C₆H₄F₅)₂(bopy-N,O)], whereas for cis-[Pt(C₆H₄F₅)₂(bopy-N)(PPh₃)] it is 1681 cm⁻¹ and is 1670 cm⁻¹ for the free ligand. This observation has been previously reported for other ligands containing ketonic C=O groups able to coordinate to metal centers (3). The reason for the decrease in the frequency of the stretching absorption of the C=O bond is that the electron donation of the oxygen atom to the metal center in the chelating situation causes the C=O bond to weaken.

Bearing this in mind, we have developed the synthesis of [PdCl₂(bopy-N,O)] (1) and the study of its reactivity towards some simple ligands. The structure of the resulting complexes can easily be derived from their infrared spectra, especially the v(CO) absorption. The general process for the preparation of complexes 1–4 is shown in Scheme I. We think that this series of reactions can constitute two or three sessions of an inorganic chemistry experimental course for undergraduates. The synthetic laboratory work involved is not complicated, and the use of a quick and commonly available spectroscopic technique such as infrared spectroscopy allows the structure of the complexes obtained to be determined without any difficulty.

Discussion

The salt PdCl₂ is a reddish brown powder, which is insoluble in most of the usual solvents. As expected, its infrared spectrum shows one strong absorption at 340 cm⁻¹ corresponding to the ν(Pd−Cl) bond. When an equimolar mixture of PdCl₂ and the bopy ligand is refluxed in acetone (6 hours), tetrahydrofuran (4 hours), or anisol (methyl phenyl ether, 3 hours), a change in the color of the suspension from the reddish brown of the starting material to the orange solid of the complex 1 can be observed. Complex 1 can be obtained by filtration of the resulting suspension (89% yield). If the reaction is run at room temperature, even with several days of stirring, or is refluxed during shorter times, only mixtures of 1, PdCl₂, and cis-[PdCl₂(bopy-N)], (2) are obtained. These compounds cannot be easily separated owing to their insolubility in common solvents. As described below, 2 can be prepared intentionally in good yield using 1 as starting material. Neither mixtures nor decomposition is observed when the suspension is refluxed for longer periods (36 hours in acetone) or stirred at room temperature for a week after the refluxing time; in these conditions only complex 1 is obtained. The use of solvents such as methanol, ethanol, or isopropanol as solvents causes the reduction of PdCl₂ to Pd(0).

The infrared spectrum of 1 contains numerous signals, most of which correspond to internal vibrations of the bopy ligand (2). The most interesting one for our study is the strong ν(CO) absorption that appears at 1537 cm⁻¹. This

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PdCl₂ + \text{bopy} \rightarrow \text{Me}_2CO \rightarrow \text{Reflux}
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\[
\nu(CO) = 1670 \text{ cm}^{-1}
\]

\[
\nu(CO) = 1537 \text{ cm}^{-1}
\]

Scheme I

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value represents a shift to a lower frequency of 133 cm⁻¹ with respect to the free ligand, indicating the coordination in a chelate fashion of the bory molecule. Other informative signals in the infrared spectrum of 1 are the v(Pd-C1) absorptions that appear at 346 and 338 cm⁻¹ (C₈, 2A). Complex cis-[PdCl₂(bipy-N,N)] (2) can be prepared by adding an equimolar amount of bipy ligand to a suspension of 1 in aceton. After 1 hour of stirring the suspension turns yellow and the filtration renders 2 as a yellow solid with 65% yield. The use of an excess of bipy (4-fold) does not have any effect on the preparation of 2, and the unreacted ligand remains in the acetone solution after filtration.

The infrared spectrum of 2 shows a displacement of the v(CO) signal towards a higher frequency compared to the situation for 1. Absorption now appears at 1679 cm⁻¹, which is a similar value to that found in the free ligand spectrum, thus indicating that the oxygen atom of the ketonic group is no longer bonded to the palladium center. This result clearly shows that the Pd–O–C bond is weak and easily displaced by the pyridine nitrogen atom, establishing a stronger Pd–N bond.

A similar result is obtained when 1 is reacted with the equimolecular amount of PPh₃. The addition of the phosphine ligand to a suspension of 1 in aceton causes the orange solid to dissolve almost immediately producing a yellow solution. The complete evaporation of the solvent and the addition of n-hexane to the yellow residue render the complex cis-[PdCl₂(bipy-N)(PPh₃)] (3) in 78% yield. The infrared spectrum of 3 once again indicates that the oxygen atom has been replaced by the phosphorous atom of the PPh₃ ligand and a Pd–O–C bond is no longer present, since the v(CO) signal appears at 1673 cm⁻¹ in the region of the noncoordinated ketonic group. An excess of PPh₃ causes the complete displacement of the bipy ligand and formation of [PdCl₂(PPh₃)₂], which is insoluble in acetone.

The addition of amionic ligands to 1 has the same effect. When an excess (1:2 molar ratio) of NMe₄Cl is added to a suspension of 1 in methyl alcohol and the mixture is stirred for 1 hour, a change in color from orange to yellow is observed. The mixture is filtered off and the resulting yellow solid is identified as the complex [NMe₄][PdCl₂(bipy-N)] (4) (62% yield). The excess of NMe₄Cl remains in the filtrate. The infrared spectrum shows a signal at 1670 cm⁻¹, thus indicating the replacement of the oxygen atom by the chloride anion in the coordination sphere of the metal center. The difference in the relative strength of the Pd–N and Pd–O bonds is worth of mention, given that the excess of chloride ligand in the reaction is not able to cleave the pyridinic bond.

Another interesting feature in the infrared spectra of complexes 2–4 is the presence of absorptions due to v(Pd–Cl) 358 (sh), 350 cm⁻¹ (C₁, A + B; or if C₁, A + A' for 2, 367 and 357 cm⁻¹ (C₈, 2A) for 3, and as a split signal 348, 333, and 320 cm⁻¹ (C₈, 2A + A') for 4.

As additional exercises we suggest two questions related to the experiment that can be proposed to the students.

1. Give a reason for the variation of the frequency of the absorption v(CO) in complexes 2–3 with respect to that observed for 1. Why is the value of the frequency lower for 1 than for 2–3?
2. Together with the absorption v(CO), the observation of the v(Pd–Cl) in these complexes provides some interesting structural information. Propose the structures of the prepared complexes by studying the patterns of the signals v(Pd–Cl) on the basis of the group theory and normal modes of vibration that would be expected for these complexes.

**Experimental Procedure**

PdCl₂ and 2-benzoylpyridine (Aldrich) were obtained from commercial sources and used as delivered. Infrared spectra were recorded over the range of 200–4000 cm⁻¹ in a Perkin-Elmer 883 spectrophotometer from Nujol mulls between polyethylene sheets. For complexes 1–4, C, H, and N analyses were performed with a Perkin-Elmer 2400 microanalyzer. The amounts of the starting materials are just suggestions. Similar yields to those described below have been obtained on a small scale, using 0.100 g. Nevertheless, it must be noted that 1 is used as the starting material in the syntheses of 2–4, and therefore, an adequate quantity of 1 must be obtained.

**Preparation of [PdCl₂(bipy-N,N,O)] (1)**

A mixture of 0.500 g (2.820 mmol) of PdCl₂ and 0.517 g (2.820 mmol) of 2-benzoylpyridine in 60 ml of acetone was refluxed and stirred for 6 hours. After that, the orange solid formed was filtered off and identified as [PdCl₂(bipy-N,N,O)] (1), 88% yield. A yield of 82% was obtained when the amounts of the reaction were scaled to 0.100 g (0.561 mmol) of PdCl₂ as the starting material. Anal. found (calcld): C 39.71(39.98), H 2.37 (2.52), N 3.68 (3.89).

**Preparation of cis-[PdCl₂(bipy-N)] (2)**

To a suspension of 0.150 g of 1 (0.416 mmol) in 40 ml of acetone, 0.076 g (0.416 mmol) of bipy was added and the mixture was stirred at room temperature during 1 hour. After this period the suspension was filtered off giving rise to cis-[PdCl₂(bipy-N,N)] (2) as a yellow solid, 65% yield. Anal. found (calcld): C 52.69 (53.02), H 3.21 (3.34), N 5.13 (5.15).

**Preparation of cis-[PdCl₂(bipy-N)(PPh₃)] (3)**

To a suspension of 0.150 g of 1 (0.416 mmol) in 40 ml of acetone, 0.109 g (0.416 mmol) of PPh₃ was added and the complete solution of the reactants was observed. The solution was stirred for 15 minutes at room temperature and then evaporated to dryness. The residue was treated with ca. 20 ml of n-hexane, rendering complex cis-[PdCl₂(bipy-N)(PPh₃)] (3) as a yellow solid, 78% yield. Anal. found (calcld): C 57.61 (57.66), H 3.92 (3.88), N 2.13 (2.25).

**Preparation of [NMe₄][PdCl₂(bipy-N)] (4)**

To a suspension of 0.150 g of 1 (0.416 mmol) in 40 ml of MeOH, 0.092 g (0.832 mmol) of NMe₄Cl was added. The mixture was stirred during 1 hour at room temperature and then evaporated. The yellow solid formed was filtered off and identified as [NMe₄][PdCl₂(bipy-N)] (4), 62% yield. Anal. found (calcld): C 40.35 (40.88), H 4.76 (4.50), N 5.89 (5.96).

**Literature Cited**

