

Article

Ligand Interchange from Bis(3,3-Pentamethylenediaziridine)Cobalt Dichloride. Evidence of Metallacyclic Heterobimetallic Intermediate Formation

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O intercâmbio de ligantes pode ser observado em reações de dicloreto de cobalto bis(3,3-pentametilenediaziridina) com os cloretos de Pd(II), Cd(II), Ni(II) e Rh(III). No caso da reação com dicloreto de paladiobis(benzonitrila) a estereoquímica do produto isolado indica que o intermediário envolvido nesta reação é um complexo metalacíclico heterobimetalico que, dependendo da combinação de metais, pode ser isolado.

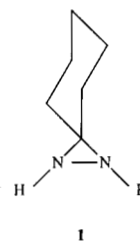
Ligand interchange can be observed in reactions of bis(3,3-pentamethylenediaziridine)cobalt dichloride with Pd(II), Cd(II), Ni(II) and Rh(III) chlorides. In the case of the reaction with bis(benzonitrile)palladium dichloride the stereochemistry of the product isolated indicates that the intermediate involved in this reaction is a metallacyclic heterobimetallic complex which, depending on the combination of the metals, can be isolated.

Keywords: ligand interchange, metallacyclic, heterobimetallic

Introduction

3,3-pentamethylenediaziridine, **I**, reacts with cobalt(II), palladium(II), nickel(II) and rhodium(III) chlorides forming the corresponding complexes in which the heterocycle coordinates to the metal by only one nitrogen atom¹. In these compounds the nature of the metal and the geometry or stereochemistry around the metal do not affect the stability of the complexes; in all cases the ring system of the heterocycle is preserved after coordination. This shows that these transition metals are unable to promote the rupture of the strained ring system. In the solid state these complexes are stable and can be stored for several months without decomposition. Most of these compounds are insoluble in common organic solvents, but in the case of the cobalt(II) and palladium(II) compounds, which are soluble in dimethylsulfoxide, the ¹H-NMR data indicate that in solution the heterocycle does not dissociate from the metal¹.

In all diaziridine complexes isolated to date we have observed that although the heterocycle could act as a bidentate ligand, it coordinates to different transition metals by only one nitrogen atom, independent of the reaction conditions. This



prompted us to study different combinations of metals in order to investigate whether complexes having the heterocycle bound to two different metals could be prepared.

Results and Discussion

In the reaction of bis(3,3-pentamethylenediaziridine)cobalt dichloride, **2a**, with cadmium dichloride, we observed the appearance of a white precipitate in the initially blue solution, which was isolated after stirring for 3 h. This product oxidizes iodide to iodine which is clear evidence that the ring system of the heterocycle was preserved². The data from the elemental analysis indicate only two molecules of the diaziridine per cadmium atom in the product. Similarly, in the stoichiometric reaction of cad-

mium dichloride with **1** at room temperature we observed the formation of the same product isolated in the reaction of **2a** with cadmium dichloride. This product was identified as the tetrahedral complex bis(3,3-pentamethylenediaziridine)cadmium dichloride, **2b**, which is insoluble in common organic solvents and is not described in the literature.

Based on these data we conclude that in the reaction of **2a** and cadmium dichloride the interchange of the diaziridine molecules occurred between the two metals. At the end of the reaction, the cobalt present in **2a** was recovered quantitatively as cobalt dichloride, as shown by atomic absorption measurements.

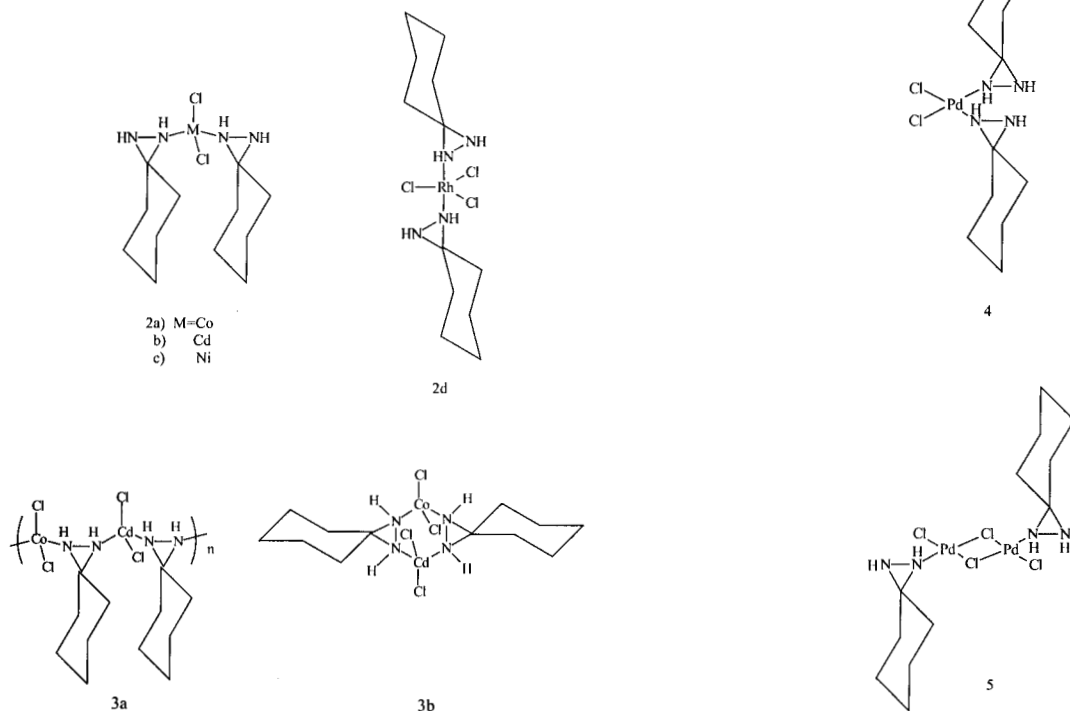
This reaction might occur through an intermediate containing both metals simultaneously bound to the same diaziridine molecule, since there is no free heterocycle in solution, as observed by $^1\text{H}\{^{13}\text{C}\}$ NMR measurements of solutions of complexes formed from **1** and Pd(II), Ni(II), Rh(III) and Co(II) chlorides. In this way, the formation of intermediates such as **3a** and/or **3b** is possible, in which the geometry around both metals is tetrahedral and, after the rupture of two Co-N bonds, leads to the formation of **2b**. The isolation and purification of **2b** from CoCl_2 is very easy since it is insoluble in common organic solvents. However, it is not possible to decide whether it is structure **3a** or **3b** which is involved in the ligand interchange from **2a**, as both lead to the same product.

This ligand interchange from complex **2a** was extended to nickel(II) and rhodium(III) chlorides, and the products **2c** and **2d** were easily and quantitatively isolated from the reaction mixture. These products were identified by com-

parison with authentic samples prepared according to previously described methods¹. Again, it was not possible to decide which kind of intermediate (oligomeric or metalacyclic) is involved in these ligand interchanges from complex **2a**.

On the other hand, in the reaction involving **2a** and bis(benzonitrile)palladium dichloride, the initially blue solution became green with a slow and continuous formation of a yellow solid. After stirring for 3 h at room temperature, a yellow solid was separated from the blue solution, and this product is capable of oxidizing iodide to iodine, which is evidence that the ring system of the heterocycle was preserved². The data from the elemental analysis indicate two diaziridine molecules per palladium atom, showing that this product is different from **5**, which is obtained by a direct reaction between **1** and bis(benzonitrile)palladium dichloride¹. In the IR spectra the product shows two bands for the Pd-N bond and two for the Pd-Cl bond. According to the literature³, square planar complexes of palladium(II) with two chlorides and two nitrogenated ligands, which show two bands in the $400\text{-}500\text{ cm}^{-1}$ region for the Pd-N bonds and two bands in the $310\text{-}380\text{ cm}^{-1}$ region for the Pd-Cl bonds, present *cis* stereochemistry around the palladium atom. These data are in agreement with structure **4** for the ligand interchange product from **2a** and bis(benzonitrile)palladium dichloride.

Analogous to the behavior of 3,3-pentamethylenediaziridine in its reaction with bis(benzonitrile)palladium di-



chloride¹, the formation of intermediate **6** could occur from **2a** and bis(benzonitrile)palladium dichloride, although the formation of **4** would not be possible after the rupture of the Co-N bonds.

In the same way, we could assume the formation of **7** from **2a** and bis(benzonitrile)palladium dichloride. However, the starting palladium complex presents a *trans* stereochemistry, and according to the literature⁵ for reactions involving nitrogenated heterocycles and palladium(II) compounds, starting from a complex with *trans* stereochemistry, the product will show the same stereochemistry as that of the starting complex. As such, the formation of **7** is not possible in this reaction.

According to these considerations we propose that the palladium atom must coordinate to nitrogen atoms from two diaziridine molecules bound to the same cobalt atom. This would force the two chlorides to assume adjacent positions, making the stereochemistry around the palladium atom *cis*. The intermediate **8** is a six membered metallacyclic heterobimetallic compound from which the formation of **4** occurs after the rupture of two Co-N bonds.

The complex *cis*-bis(3,3-pentamethylenediaziridine)palladium dichloride, **4**, is air stable and can be stored for long periods without decomposition. To date, this compound has not been described in the literature. It should be noted that this is a good procedure for obtaining *cis*-palladium(II) compounds from *trans* starting reagents and monodentate ligands.

These interchange reactions go to completion after stirring for 3 h at room temperature, and are very easy to follow because the products are insoluble and present a different color than the solutions from which they are formed. As no free diaziridine is found in solution, the only possible way to form the products is with the presence of a heterobimetallic intermediate in which the heterocycles are simultaneously bound to two different metals.

In an attempt to isolate the intermediate involved in the formation of **4**, we stopped the reaction between **2a** and bis(benzonitrile)palladium dichloride after 30 min of stirring. The solvent was removed and a yellow solid was obtained. It was washed several times with chloroform and light petroleum ether. The elemental analysis indicated two

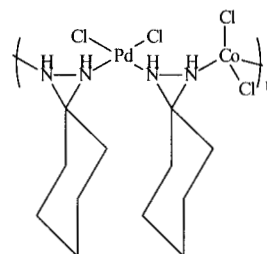
diaziridine molecules, PdCl₂ and CoCl₂. This product shows IR spectra in the region 400-600 cm⁻¹, very similar to that of **4**. It is soluble in acetone, and after a few minutes in this solution a yellow solid starts to precipitate, which forms complex **4** in a quantitative yield. Unfortunately, due to its instability in solution and the paramagnetism of Co(II), it was not possible to obtain NMR data for this intermediate which we believe has structure **8**.

It seems that the weak interaction between cobalt and the nitrogen of 3,3-pentamethylenediaziridine allows these ligand interchanges to occur. Evidence to support this was obtained from the reaction between **2b,c** and **4** with cobalt dichloride, in which, after stirring 8 h, the starting reagents were recovered unaltered.

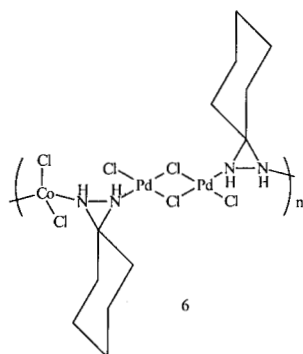
These results show that ligand interchange can occur depending on the nature of the metal involved and/or its ability to coordinate to the heterocycle. These reactions are consistent with the possible mechanism leading to the formation of a heterobimetallic intermediate which, according to the combination of metals used, can be isolated, as was the case with palladium and cobalt.

Experimental Details

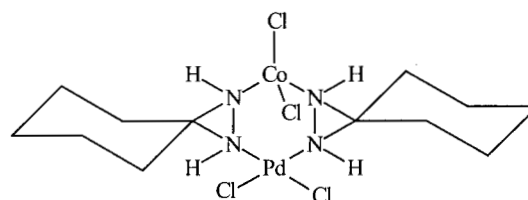
Bis(3,3-pentamethylenediaziridine)cobalt dichloride and bis(benzonitrile)palladium dichloride were prepared according to procedures described in the literature^{1,6}. IR spectra were measured on a JASCO IR 700 spectrometer. Elemental analyses were performed on a Perkin-Elmer 2400 CHN Elemental Analyser. Atomic Absorption measurements were performed on a Perkin-Elmer mod. 5000 spectrometer. All melting points are uncorrected.



7



6



8

Synthesis of bis(3,3-pentamethylenediaziridine)cadmium dichloride, 2b

A solution of 3,3-pentamethylenediaziridine (0.22 g, 2.0 mmol) in methanol (10 mL) was slowly added to a solution of cadmium dichloride (0.18 g, 1.0 mmol) in methanol (20 mL). The solution was stirred for 3 h at room temperature during which time the appearance of a white precipitate was observed. The solution was filtered and the white product was washed with light petroleum ether (30 mL) and dried under vacuum. **2b** was obtained as a white powder in a quantitative yield. M.p. > 250°. IR (KBr) 3194 and 3176 cm⁻¹. (Found C,35.40; H,5.87; N,13.69. C₁₂H₂₄N₄Cl₂Cd requires C,35.45; H,5.90; N,13.78 %).

Reaction between bis(3,3-pentamethylenediaziridine)cobalt dichloride and cadmium(II), nickel(II) or rhodium(III) chlorides. General procedure

In a round-bottomed flask containing acetone (25 mL), bis(3,3-pentamethylenediaziridine)cobalt dichloride (0.35 g, 1.0 mmol) was introduced and the resulting blue solution was kept under magnetic stirring at room temperature. Cadmium, nickel or rhodium chloride (1.0 mmol), previously dissolved in methanol (10 mL), was added to the flask giving a clear blue solution. During stirring the appearance of a precipitate was observed, which was filtered after 3 h and washed with chloroform (20 mL) and light petroleum ether (30 mL) and dried under vacuum. **2b**, **2c** and **2d** were obtained as powders in quantitative yields. These products were identified by IR spectroscopy, elemental analysis, and by comparison with authentic samples¹.

The filtered blue solution was evaporated and the resulting blue powder was identified as CoCl₂ by precipitation with silver nitrate and by atomic absorption spectrometry.

Reaction of bis(3,3-pentamethylenediaziridine)cobalt dichloride with bis(benzonitrile)palladium dichloride

A solution of bis(benzonitrile)palladium dichloride (0.38 g, 1.0 mmol) in acetone (10 mL) was added to a solution of bis(3,3-pentamethylenediaziridine)cobalt dichloride (0.35 g, 1.0 mmol) in acetone (30 mL), giving a green solution. This solution was kept under magnetic stirring and a slow and continuous formation of a yellow precipitate was observed. After 3 h at room temperature the yellow precipitate was filtered off, washed with light petroleum ether (30 mL), and dried under vacuum for 3 h. **4** was obtained as a yellow powder in quantitative yield. M.p. 194°. IR(nujol) 3200, 482, 451, 349, 313 cm⁻¹. (Found C,35.79; H,5.43; N,13.52. C₁₂H₂₄N₄Cl₂Pd requires C,35.87; H,5.98; N,13.95%).

Isolation of 8 from bis(3,3-pentamethylenediaziridine)cobalt dichloride and bis(benzonitrile)palladium dichloride

A solution of bis(benzonitrile) palladium dichloride (0.38 g, 1.0 mmol) in acetone (10 mL) was added to a solution of bis(3,3-pentamethylenediaziridine)cobalt dichloride (0.35 g, 1.0 mmol) in acetone (30 mL) at 0°, giving a clear green solution, which was kept at this temperature under magnetic stirring for 30 min. After this time the solution was filtered and evaporated under reduced pressure to give a yellow solid in a 90% yield. M.p. > 250°. IR (nujol) 3204, 3176, 440, 472, 340, 310, 260 cm⁻¹. (Found C,27.05; H,4.40; N,10.41. C₁₂H₂₄N₄Cl₄CoPd requires C,27.10; H,4.51; N,10.54%).

Reaction of 2b, 2c, 2d and 4 with cobalt dichloride

In a round-bottomed flask containing acetone (25 mL) **2b**, **2c**, **2d** or **4** (1.0 mmol) was introduced, and the resulting mixture was kept under magnetic stirring at room temperature. Cobalt dichloride (1.0 mmol) dissolved in acetone (10 mL) was added to the flask, and the mixture was stirred for 8 h at room temperature. At the end of this time the solution was filtered off, the solvent was evaporated, and methanol (10 mL) was added, giving a blue solution. The solution was filtered again and methanol was evaporated, giving a blue powder (0.13 g) presenting 45.9% cobalt (determined by atomic absorption spectrometry; CoCl₂ requires 46.10% cobalt). This was dissolved in water giving a pink solution, and then a white precipitate upon the addition of aqueous silver nitrate solution. These results indicate that at the end of the reaction cobalt was recovered quantitatively as unchanged CoCl₂.

Acknowledgments

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