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COMMUNICATION

NEW ROUTES FOR THE SYNTHESIS OF CHLORO(DIETHYLENETRIAMINE)PLATINUM(II)CHLORIDE AND CHLORO(2,2′:6′,2″-TERPYRIDINE)PLATINUM(II) CHLORIDE DIHYDRATE

GIULIANO ANNIBALE,* MATILDE BRANDOLISIO and BRUNO PITTERI

Dipartimento di Chimica, Università di Venezia, Calle Larga S. Marta 2137, 30123-Venezia, Italy

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Abstract—[Pt(dien)Cl]Cl (dien = diethylenetriamine) has been obtained in high yield (>90%) by interaction of *cis*-$[Pt(dmso)_2Cl_2]$ (dmso = dimethylsulfoxide) with the triamine in methanol. The same method, when applied to 2,2′:6′,2″-terpyridine (terpy), gave a mixture of $[Pt(terpy)Cl][Pt(dmso)Cl_3]$ and $[Pt(terpy)Cl]Cl \cdot 2H_2O$. The latter complex has been obtained in nearly quantitative yield by interaction of equimolar amounts of $[Pt(COD)Cl_2]$ (COD = 1,5-cyclooctadiene) and terpy in water.

Coordination compounds of platinum(II) and palladium(II) with the tridentate ligands diethylenetriamine (dien) and 2,2′:6′,2″-terpyridine (terpy) have provided useful substrates for kinetic studies in substitution reactions at planar four-coordinate complexes. Moreover there has been recently much interest in terpy complexes in connection with their properties as metallointercalators to nucleic acids[1] as well as their intriguing spectroscopic and photophysical behaviour.[2]

Hitherto the reported procedures for the preparation of the platinum(II) chloro derivatives, namely [Pt(dien)Cl]Cl[3] and $[Pt(terpy)Cl]Cl \cdot nH_2O$ ($n = 2, 3$),[4–6] are rather laborious (for the former compound) and time consuming (for the latter). Recently $[Pt(terpy)Cl]Cl \cdot 3H_2O$ has been obtained in 47% yield using microwave dielectric loss heating effects.[7]

In this communication we report novel preparative methods which readily give the above complexes in high yield. The starting reacting compounds, *cis*-$[Pt(dmso)_2Cl_2]$[8] (dmso = dimethylsulfoxide) and $[Pt(COD)Cl_2]$[9] (COD = 1,5-cyclooctadiene), can be easily prepared in nearly quantitative yield by well established procedures.

RESULTS AND DISCUSSION

Details of the preparations are given in the Experimental section.

Chloro(diethylenetriamine)platinum(II)*chloride*, [Pt(dien)Cl]Cl (**1**)

Watt and Cude[3] prepared compound **1** by reacting silver chloride with the iodo-derivative [Pt(dien)I]I, which in turn was obtained by interaction of $PtI_2 \cdot H_2O$ with the triamine in water.

We have found that the complex can be readily synthesized in high yield by simply allowing *cis*-$[Pt(dmso)_2Cl_2]$ to react with an equimolar amount of dien in methanol. Owing to the high *trans*-labilizing effect of dmso,[10] the reaction goes rapidly to completion in refluxing methanol. Previous findings on the reaction between *cis*-$[Pt(dmso)_2Cl_2]$ with mono-[11] and bi-dentate[12] nitrogen donors suggest that the reaction proceeds through formation of the labile $[Pt(dien)dmso]^{2+}$ intermediate, which is

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* Author to whom correspondence should be addressed.

known to undergo easy replacement of coordinate dmso by chloride ions.[13] The infrared spectrum of **1** is in close agreement with that reported by Watt and Cude,[3] and its analytical data are satisfactory.

Chloro(2,2′ : 6′,2″-*terpyridine*)*platinum*(II)*chloride dihydrate*, [Pt(terpy)Cl]Cl · $2H_2O$ (**2**)

The reaction of K_2PtCl_4 with terpy in water has been reported to afford both [Pt(terpy)Cl]Cl, which could be isolated as the dihydrate (**2**) or trihydrate, and $[Pt(terpy)Cl]_2[PtCl_4]$ (**3**), the latter being the major reaction product.[4,5] The yield of **2** was increased to about 70% by refluxing the reaction mixture for 20–100 h.[6]

In our research, even starting from platinum chloride or dichlorobis(benzonitrile)platinum(II) in dimethylformamide, the very insoluble Magnus-type salt **3** formed in much larger quantity than **2**.

The same reaction employed for the preparation of **1**, namely *cis*-$[Pt(dmso)_2Cl_2]$ with terpy in methanol, was also tested. In this case however, besides the desired compound **2**, the salt [Pt(terpy)Cl]$[Pt(dmso)Cl_3]$ (**4**) was also formed (see Experimental section). The failure of obtaining the only [Pt(terpy)Cl]Cl is a consequence of the almost complete insolubility of **4** which subtracts the $[Pt(dmso)Cl_3]^-$ anion formed by reaction (1).

$$cis\text{-}[Pt(dmso)_2Cl_2]+Cl^- \rightarrow [Pt(dmso)Cl_3]^- + dmso \quad (1)$$

Pure **2** can be easily obtained in a few minutes and nearly quantitative yield by reacting equimolar amounts of $[Pt(COD)Cl_2]$ and terpy in water at 40–50°C. The high *trans*-labilizing effect of the coordinated diolefin and its lability when mono-coordinated to the metal ion account for the above result. The product, which is isolated in the dihydrated form by evaporating to dryness the solution, is satisfactorily pure as shown by elemental analysis. It can be recrystallized from a minimum amount of 1 M hydrochloric acid at 50°C. The electronic absorption spectrum of the compound in 0.1 M NaCl solution closely agrees with that reported in the literature.[6] The same reaction affords **2** in similar yield when methanol is used as solvent. In this case the product which precipitates from the solution by addition of diethyl ether, is yellow and becomes red–orange when washed with diethyl ether and air dried. Similar variations of colour on changing the method of precipitation and crystallization have been already observed.[2] No reaction occurred between $[Pt(COD)Cl_2]$ and terpy in non water-like solvents such as nitromethane, acetonitrile, dichloromethane or tetrahydrofuran.

EXPERIMENTAL

Materials

Dipotassium tetrachloroplatinate(II) was prepared from platinum metal by a standard method.[14] Dimethylsulfoxide, 1,5-cyclooctadiene, diethylenetriamine, 2,2′ : 6′,2″-terpyridine, the inorganic salts, and solvents were reagent grade products. *Cis*-$[Pt(dmso)_2Cl_2]$[8] and $[Pt(COD)Cl_2]$[9] were prepared as described in the literature.

Preparation of [Pt(dien)Cl]Cl (**1**)

A solution of (dien) (0.073 g, 0.71 mmol) in methanol (10 cm^3) was added with stirring to a suspension of *cis*-$[Pt(dmso)_2Cl_2]$ (0.30 g, 0.71 mmol) in methanol (50 cm^3), and the mixture was refluxed for *ca* 1 h. The resulting clear solution was concentrated in a rotary evaporator to *ca* 5 cm^3, cooled at room temperature and filtered to remove any unreacted *cis*-$[Pt(dmso)_2Cl_2]$. Chloroform (30 cm^3) was then added to precipitate the product as a gelatinous white solid which became powdery on stirring. It was filtered off, washed with chloroform, diethyl ether, air dried, and recrystallized from a filtered aqueous solution (2 cm^3) by careful addition of acetone. It was finally washed with acetone, diethyl ether and dried *in vacuo* over P_2O_5. Yield: 0.25 g, 94%. Found: C, 13.4; H, 3.3; N, 11.1. Calc. for $C_4H_{13}Cl_2N_3Pt$: C, 13.0; H, 3.6; N, 11.4%.

The reaction of cis-$[Pt(dmso)_2Cl_2]$ *with terpy in methanol*

To a stirred suspension of *cis*-$[Pt(dmso)_2Cl_2]$ (0.30 g, 0.71 mmol) in methanol (50 cm^3), a solution of terpy (0.17 g, 0.73 mmol) in the same solvent (10 cm^3) was added and the resulting mixture refluxed. After a few minutes (*ca* 10) the solution became orange and fine red–cherry crystals were deposited. Refluxing was continued for an additional hour to ensure completion of the reaction. After concentration to 10 cm^3 under reduced pressure, the red–cherry needles were collected by filtration, washed with methanol (20 cm^3) and diethyl ether, and air dried. Yield: 0.16 g (**4**, 0.2 mmol); (IR), $\nu(S{=}O)$ at 1149 cm^{-1}. Found: C, 24.5; H, 2.1; N, 4.8. Calc. for $C_{17}H_{17}Cl_4N_3OSPt_2$: C, 24.2; H, 2.0; N, 5.0%. The mother liquor plus the methanolic washings were concentrated to *ca* 10 cm^3 and then treated with diethyl ether (30 cm^3) on obtaining a yellow precipitate which was filtered off and turned red–orange on washing with diethyl ether and air drying. Yield: 0.11 g (**2**, 0.21 mmol). Found: C, 33.7; H, 2.8; N, 7.6. Calc. for $C_{15}H_{15}Cl_2N_3O_2Pt$: C, 33.7; H, 2.8; N, 7.8%.

Preparation of [Pt(terpy)Cl]Cl·$2H_2O$ (**2**)

To a suspension of [Pt(COD)Cl_2] (0.15 g, 0.40 mmol) in water (10 cm^3), terpy (0.094 g, 0.40 mmol) was added with stirring and the mixture warmed at 40–50°C. After 15 min all the solid dissolved and a red–orange clear solution was obtained which was cooled at room temperature and then filtered to remove unreacted COD-complex if any. Water was then removed under reduced pressure leaving a red–orange solid which was collected and washed thoroughly with diethyl ether and air dried. Yield: 0.21g, 98%. Found: C, 33.8; H, 2.5; N, 7.7. Calc. for $C_{15}H_{15}Cl_2N_3O_2Pt$: C, 33.7; H, 2.8; N, 7.8%. IR absorptions in the 250–3800 cm^{-1} range (KBr pellets): 3400sb, 3050mb, 1658m, 1606s, 1476s, 1453s, 1439m, 1401s, 1316m, 1284m, 1246mb, 1242w, 1092w, 1032m, 779vs, 722m, 520m, 463m, 436w, 367m, 343s, 293s cm^{-1}. UV absorptions (freshly prepared solutions in H_2O 200–400 nm): 248, 278, 327, 343 nm.

Physical measurements

IR and electronic spectra were recorded using Perkin–Elmer 683 and Perkin–Elmer Lambda 5 spectrophotometers, respectively.

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