Journal of Organometallic Chemistry, 396 (1990) 115–120
Elsevier Sequoia S.A., Lausanne

JOM 21002

Transfer of chelate ligands between platinum complexes

Enrico Rotondo, Antonino Giannetto and Santo Lanza *

Dipartimento di Chimica Inorganica e Struttura Molecolare, Università di Messina, Villaggio Sant'Agata, 98100 Messina (Italy)

(Received March 29th, 1990)

Abstract

$Me_2Pt(bt)$ (bt = 2,2′-bithiazoline N,N'-coordinated) undergoes oxidative addition of CH_2Cl_2, CH_2Br_2 and MeI. The octahedral triorganoplatinum(IV) products react with *cis*-$Pt(dmso)_2Cl_2$ to give, through the transfer of the chelate ligand bt, the complex $Pt(bt)Cl_2$ and an isomeric mixture of bis-dmso triorganoplatinum (IV) complexes.

Introduction

Use of a binucleating ligand offer an opportunity to investigate the mutual influence of two metal centres through the ligand. It has been previously shown that the transmission of electronic effect between the two metals depends on the size, steric conformation, and degree of unsaturation of the binucleating ligand. The shift of the metal to ligand charge transfer (MLCT) band in the UV-VIS spectrum as well as variations in the reactivity towards oxidative addition of the bridged metals are a consequence of such a mutual interaction [1].

We previously prepared a series of homo and heterobimetallic complexes of platinum containing the binucleating ligands 2,2′-bipyrimidine, 2,2′-bithiazoline and 2,2′-bithiazine [2]. Unfortunately, the characterization of such a kind of compounds, expecially homobimetallic compounds, is seriously restricted by their low solubility. In a search for homobimetallic complexes of platinum(II) with higher solubility, we treated $Me_2Pt(bt)$ (bt = 2,2′-bithiazoline N,N'-coordinated) with *cis*-$Pt(dmso)_2Cl_2$ in dichloromethane. The unexpected results of this and similar reactions are here reported.

Results and discussion

When $Pt(bt)Me_2$ and *cis*-$Pt(dmso)_2Cl_2$ were mixed in dichloromethane, spectroscopic monitoring revealed an unexpected two-step process (Fig. 1). The first step

0022-328X/90/$03.50

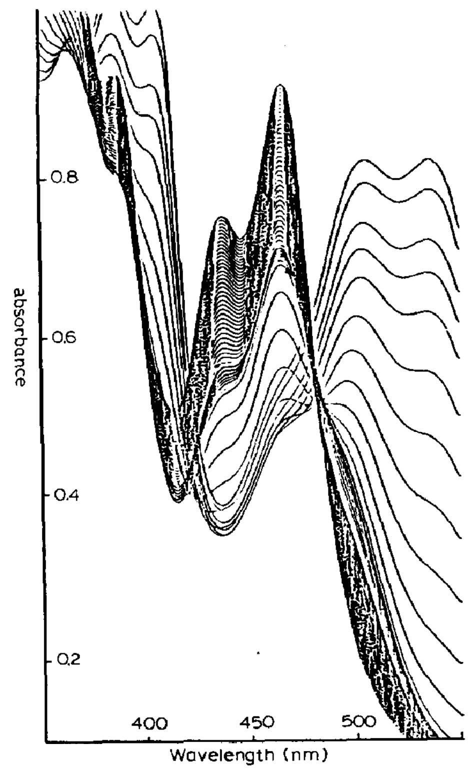


Fig. 1. Changes in the UV-VIS spectrum (350–550 nm) during the reaction: *cis*-Pt(dmso)$_2$Cl$_2$ + PtMe$_2$(bt) in CH$_2$Cl$_2$. Scanning time 30 min for both steps.

involves the progressive disappearance of the MLCT band of Pt(bt)Me$_2$. In the absence of *cis*-Pt(dmso)$_2$Cl$_2$ the reaction stops at this stage and when it was carried out on a preparative scale *trans*-PtMe$_2$(bt)(CH$_2$Cl)Cl was easily separed from the small amount of its *cis* isomer. A similar example of activation of dichloromethane has been previously reported [3].

The second step revealed by the UV-VIS spectroscopic monitoring takes place only in the presence of *cis*-Pt(dmso)$_2$Cl$_2$, and involves the appearance of an electronic spectrum similar to that of the organoplatinum(II) starting substrate, with the MLCT transitions characteristic of platinum(II)-α-diimine derivatives shifted to higher frequencies. When the reaction was carried out on a preparative scale, red brown crystals were isolated and gave elemental analyses, IR, UV-VIS and NMR spectra identical with those of an authentic sample of Pt(bt)Cl$_2$. It was soon established that this reaction is a general one, in that Pt(N–N)Cl$_2$ is produced whenever any RX reacts with (N–N)PtR$_2$ substrates (where N–N denotes any α-diimine) in the presence of *cis*-Pt(dmso)$_2$Cl$_2$.

Unfortunately, the only product we have so far been able to isolate in the solid state is Pt(bt)Cl$_2$. Because of this we treated to octahedral *trans*-PtMe$_2$(bt)(R)X complexes (R = CH$_2$Cl, X = Cl; R = CH$_2$Br, X = Br; R = CH$_3$, X = I) [4] with an equimolar amount of *cis*-Pt(dmso)$_2$Cl$_2$ in CDCl$_3$ and after removing the Pt(bt)Cl$_2$, examined solutions by ^{1}H NMR spectroscopy. The spectra (Fig. 2) show that these

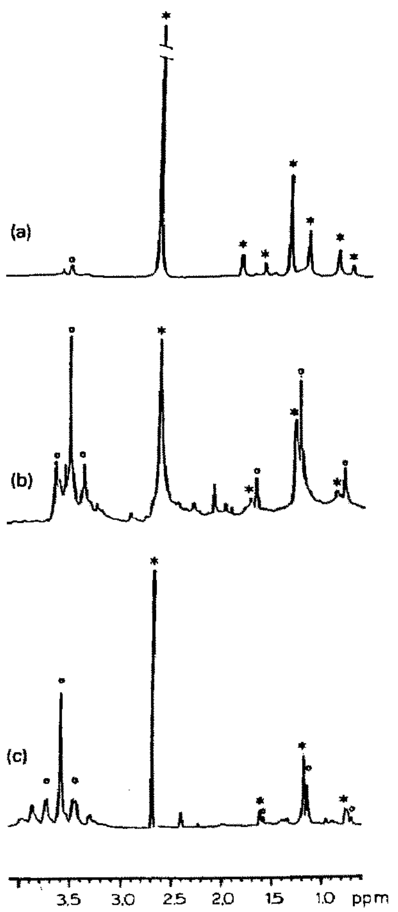
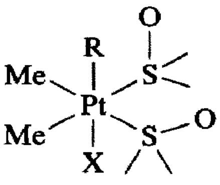
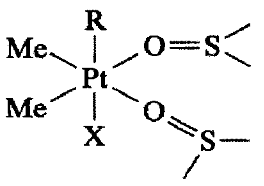


Fig. 2. ^{1}H NMR spectrum of the complexes: (a) *fac*-Me$_3$PtI(dmso)$_2$; (b) *trans*-Me$_2$Br(CH$_2$Br)(dmso)$_2$; (c) *trans*-PtMe$_2$Cl(CH$_2$Cl)(dmso)$_2$. (a) and (c) were recorded at 225 K, (b) at room temperature. (°) Isomers A; (*) isomers B (see text).

solutions mainly contain, in various ratios, two linkage isomers, denoted by **A** and **B**, which differ in the resonances for by the coordinated dmso.

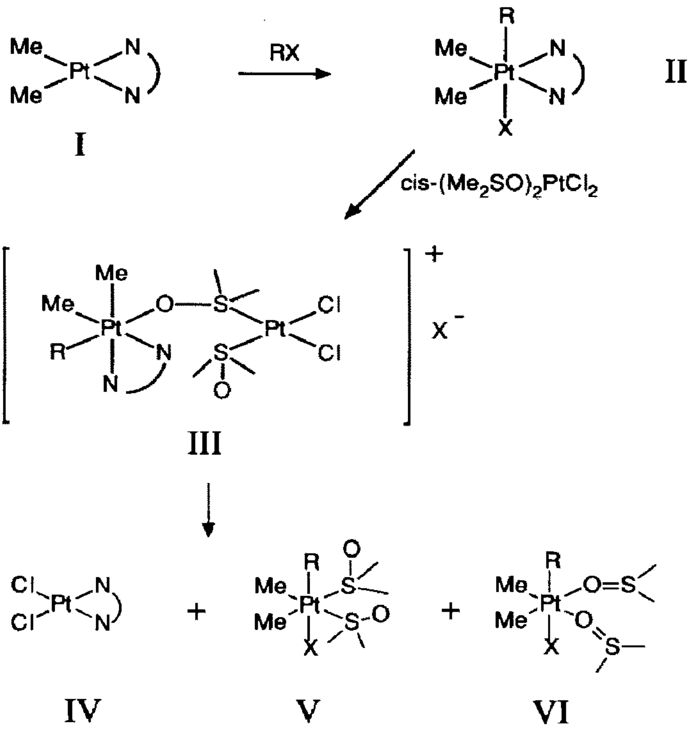


(Isomers **A**)



(Isomers **B**)

The sulphur-coordinated dmso complexes (isomers **A**) are characterized by resonances at 3.5–3.6 ppm flanked by platinum satellites in the expected 1 : 4 : 1 intensity ratio (^3J(Pt–H) = 20 Hz). The isomers **B** are characterized by resonances at 2.65–2.70 ppm. The chemical shift and the absence of platinum satellites are consistent with their formulation as oxygen-coordinated dmso derivatives [5]. The



R= -CH2Cl; X= Cl
R= -CH2Br; X= Br
R= -CH3; X= I

Scheme 1

peaks at 2.65–2.70 ppm, which are sharp at 225 K, become broad at room temperature, probably because of fast exchange with water molecules. Each isomer shows a single resonance for the two equivalent platinum-bonded methyl groups ($\delta = 1.2$–1.4 ppm, $^2J(\text{Pt–H}) = 70$ Hz), except in the case of *fac*-$\text{Me}_3\text{Pt(dmso)}_2\text{I}$, in which the two groups of non-equivalent CH_3–Pt signals (δ(Pt–Me *trans* to dmso) $= 1.33$ ppm, $^2J(\text{Pt–H}) = 79.6$ Hz; δ(Pt–Me *trans* to I) $= 1.2$ ppm, $^2J(\text{Pt–H}) = 72.9$ Hz) are not split because the type A isomer is present only in traces. Comparison of the integrals of these signals with those for the *S*-coordinated and *O*-coordinated dmso, allowed attribution of each methyl resonance to the appropriate isomer. Data for the Pt–CH_2–X resonances cannot be given in because the signals are observed covered by *S*-coordinated dmso signals. We can represent the overall process in terms of scheme 1. The suggested, and seemingly unlikely, intermediate III accounts for the following facts. First, when compounds II are treated with a bis-sulphide dichloroplatinum(II) complex no reaction takes place. This may mean that the nucleophilic attack on the Pt^{IV} species may be through the oxygen atom of *S*-coordinated sulphoxide in *cis*-$\text{Pt(dmso)}_2\text{Cl}_2$, rather than through a direct attack of the electron rich platinum(II) such as was recently described for alkyl halide transfer from palladium(IV) to platinum(II) [6]. We also observed that the presence of small amount of ($^{n}Bu_4N$)X, dramatically reduce the rate of the process, perhaps because the presence of free halide ion reverses the breaking of the Pt(IV)–X bond in II [7].

It is relevant to comment on the stereochemistry of the reaction, since the presence in the products of doubly *S*-bonded sulphoxide complexes seems to conflict with the suggestion that III is an intermediate. We suggest that the reverse attachement of X^- to III may, after the tranfer of the chelate bt, produce the doubly *O*-bonded sulphoxide complexes of Pt^{IV} together with the corresponding derivatives with mixed coordination modes for the two sulphoxides. These are probably unstable for electronic reasons (antisymbiosis) [8], and so might undergo reversible symmetrization, leading to the observed isomeric products. Steric factors may play an important role in this process. The almost complete absence of the type A isomer in $Me_3PtI(dmso)_2$ could, in fact, be due to the greater steric hindrance of I than of Cl and Br.

Finally, we mention that we attempted to confirm the structure of V and/or VI by means of an oxidative addition of MeI to *cis*-$Pt(dmso)_2Me_2$. The only product we obtained gave NMR parameters in agreement with those of the tetramer $(Me_3PtI)_4$ [9].

Experimental

All the reagents were of analytical grade and were used as purchased. Solvents were distilled over activated molecular sieves (4 Å) before use. 2,2′-Bithiazoline was made as previously described [10], as were $Pt(bt)Me_2$ [2b] and *cis*-$Pt(dmso)_2Me_2$ [11].

The IR, UV-VIS and ^{1}H NMR spectra respectively were recorded on the following instruments: PE 1720 X FT-IR, PE Lambda 5 UV/VIS, and WP 80 SY Bruker.

Preparation of compounds

trans-$PtMe_2(CH_2Cl)Cl(bt)$. A solution of $PtMe_2(bt)$ (1 mmol) in CCl_4 was set aside for 4 days, then the solution was concentrated under vacuum and hexane or ether was added. Yellow crystals of *trans*-$PtMe_2Cl(CH_2Cl)(bt)$ were obtained in 60% yield. The filtrate contained only *cis* and *trans* products, showing that the reaction with CH_2Cl_2 was quantitative. The *cis* isomer was identified from the ^{1}H NMR spectrum of the filtrate (δ(Me–Pt *trans* to Cl) = 0.48 ppm, ^3J(Pt–H) = 75 Hz; δ(Me–Pt *trans* to N) = 1.21 ppm, ^3J(Pt–H) = 77.12 Hz).

Analysis: Found: C, 22.35; H, 3.31; N, 5.85; Cl, 14.10. $C_9H_{16}Cl_2N_2S_2Pt$ calcd.: C, 22.40; H, 3.36; N, 5.80; Cl, 14.73%. ^{1}H NMR ($CDCl_3$): Pt–CH_3, s, $\delta = 1.20$ ppm, ^3J(Pt–H) = 71.8 Hz; S–CH_2, m, $\delta = 3.30$ ppm; N–CH_2, m, $\delta = 4.45$ ppm; Pt–CH_2Cl, s, $\delta = 3.55$ ppm, ^2J(Pt–H) = 42.7 Hz.

trans-$Me_2PtBr(CH_2Br)(bt)$. A solution of $Me_2Pt(bt)$ (1 mmol) in CH_3Cl was reacted with an excess (0.5 ml) of CH_2Br_2. The solution became yellow-orange in few minutes. It was kept at room temperature for 24 h, then concentrated under vacuum, and hexane was added. Yellow orange crystals of *trans*-$PtMe_2Br(CH_2Br)(bt)$ were obtained in good yield (70%).

Analysis: Found: C, 19.59; H, 2.86; N, 5.06; Br, 27.9. $C_9H_{16}Br_2N_2S_2Pt$ calcd.: C, 18.9; H, 2.80; N, 4.9; Br, 28.1%. ^1H NMR ($CDCl_3$): Pt–CH_3, s, $\delta = 1.29$ ppm, $^2J(Pt\text{–}H) = 72.0$ Hz; N–CH_2, m, $\delta = 4.57$ ppm; S–CH_2, m, $\delta = 3.81$ ppm; Pt–CH_2Br, s, $\delta = 3.38$ ppm, $^2J(Pt\text{–}H) = 42.7$ Hz.

fac-Me₃PtI(bt). A solution of $PtMe_2(bt)$ (1 mmol) in $CHCl_3$ was treated with an excess of MeI (0.5 ml). The red color changed immediately to yellow. After concentration of the solution, hexane was added and yellow crystals of $Me_3PtI(bt)$ were obtained in good yield (75%). Analysis: Found: C, 20.25; H, 3.19; N, 5.31. $C_9H_{17}IN_2S_2Pt$ calcd.: C, 20.03; H, 3.15; N, 5.19%. ^1H NMR ($CDCl_3$): 2Pt–CH_3, s, $\delta = 1.37$ ppm, $^2J(Pt\text{–}H) = 73.5$ Hz; Pt–CH_3 (*trans* to I), s, $\delta = 1.21$ ppm, $^2J(Pt\text{–}H) = 72.9$ Hz; S–CH_2, m, $\delta = 3.66$ ppm; N–CH_2, m, $\delta = 4.61$ ppm.

Pt(bt)Cl₂. (a) *cis*-$Pt(dmso)_2Cl_2$ (1 mmol) was treated with the equimolar quantity of bt in $CHCl_3$. $Pt(bt)Cl_2$ separated as a brown powder in high yield (> 75%).

(b) *trans*-$PtMe_2Pt(R)X$ (R = CH_2Cl, X = Cl; R = CH_2Br, X = Br; R = CH_3, X = I) was treated with the equimolar amount of *cis*-$Pt(dmso)_2Cl_2$. After 4 days red-brown crystals separated, and were collected and air dried.

Analysis: Found: C, 16.34; H, 1.9; N, 5.95; Cl, 15.5. $C_6H_8Cl_2N_2S_2Pt$ calcd.: C, 16.4; H, 1.82; N, 6.39; Cl, 16.2%. ^1H NMR (dimethyformamide-d_7: S–CH_2, m, $\delta = 4.06$ ppm; N–CH_2, m, $\delta = 4.72$ ppm.

(Me₃PtI)₄. A solution of *cis*-$Pt(dmso)_2Me_2$ (1 mmol) in $CHCl_3$ was treated with an excess (0.5 ml) of MeI. A black suspension was appeared formed. The mixture was kept at room temperature for 4 days, then treated with charcoal and filtered. $(Me_3PtI)_4$ was obtained after concentration (yield = 50%).

References

1 J.D. Scott and R.J. Puddephatt, Organometallics, 5 (1986) 2522.

2 (a) S. Lanza, Inorg. Chim. Acta, 75 (1983) 131; (b) S. Lanza and E. Rotondo, ibid. 205 (1988) 146; (c) G. Bruno, S. Lanza and F. Nicolò, Acta Cryst. C, 46 (1990) 765.

3 J. Kuiper, Inorg. Chem., 17 (1978) 77.

4 For a review on organoplatinum(IV) complexes see: V.K. Jain, G.S. Rao, L. Jain, Advances in Organometallic Chemistry, 27 (1986) 113.

5 F.R. Hartley, S.G. Murray and A. Wilkinson, Inorg. Chem., 28 (1989) 459.

6 K.T. Aye, A.J. Canty, M. Crespo, R.J. Puddephatt, J.D. Scott and A.A. Waltson, Inorg. Chem., 8 (1989) 1518.

7 P.K. Biers, A.J. Canty, M. Crespo, R.J. Puddephatt and J.D. Scott, Organometallics, 7 (1988) 1363.

8 J.A. Davies and F.R. Hartley, Chem. Rev., 20 (1981) 44.

9 K. Kite, J.A.S. Smith and E.J. Wilkins, J. Chem. Soc. A, (1966) 1744.

10 D.A. Tomalia and J.N. Paige, J. Org. Chem., 38 (1973) 3949.

11 C. Eaborn, K. Kundu and A. Pidcock, J. Chem. Soc., Dalton Trans., (1981) 933.