Complexes of Platinum(II) Containing 2,2′-Bithiazoline and 2,2′-Bipyrimidine as Binucleating Ligands

SANTO LANZA and ENRICO ROTONDO

Dipartimento di Chimica Inorganica e Struttura Molecolare, Università di Messina, Villaggio S. Agata, 98100 Messina, Italy

(Received October 5, 1987)

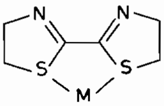
Abstract

Dimethyl and diphenyl platinum(II) complexes containing binucleating α-diimine ligands BN (BN = 2,2′-bithiazoline and 2,2′-bipyrimidine) have been isolated and characterized. Electrophilic attack of mercuric chloride on the mononuclear compounds leads to binuclear systems of C_{2v} symmetry, with the two chelating moieties of the ligands occupied by platinum and mercury, respectively. ^1H NMR spectroscopy suggests a large transmission of electronic effects between the metals through the ligands.

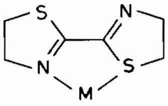
Introduction

In recent years, a great deal of attention has been attracted by the coordination modes of the bis-diimine 2,2′-bipyrimidine. The capability of such a ligand to form mono, bi and oligonuclear metal complexes, as well as its ability to transmit electronic effects between metal centres has been extensively studied [1].

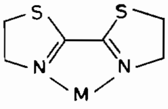
On the contrary, as regards the coordination chemistry of 2,2′-bithiazoline and related ligands [2, 3], there is, to date, relatively little information about the three possible modes of coordination to a given metal atom. Namely, 2,2′-bithiazoline could chelate a metal centre to give complexes of the type **I**, **II** or **III**. Each of these isomers can give, in principle, a bimetallic derivative.



I



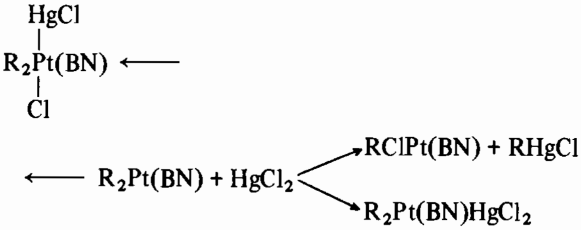
II



III

Using sulphoxide or thioether organoplatinum complexes as sources of R_2Pt units, we have prepared the mononuclear compounds $R_2Pt(BN)$ (BN = 2,2′-bithiazoline, bt, and 2,2′-bipyrimidine, bipym; R = methyl or phenyl). The first objective of the present work was to determine whether the coordination mode of 2,2′-bithiazoline to R_2Pt is **I**, **II** or **III**.

In these complexes the possible target of mercuric chloride could either be the d_{z^2} orbital of the metal centre, the metal carbon σ-bond or the lone pairs of the second chelating system still available for coordination.



$$R_2\overset{\displaystyle HgCl}{\underset{\displaystyle Cl}{Pt}}(BN) \longleftarrow R_2Pt(BN) + HgCl_2 \begin{cases} \rightarrow RClPt(BN) + RHgCl \\ \rightarrow R_2Pt(BN)HgCl_2 \end{cases}$$

Factors which influence the actual reaction path result from a delicate balance of electronic effects.

The reactions with mercuric chloride described in the present paper, invariantly lead to bimetallic compounds with the two metal centres indirectly connected through the binucleating system. These compounds have been isolated and characterized by NMR spectroscopy; NMR data emphasize a large electronic transmission through the binucleating system.

Experimental

2,2′-Bithiazoline was prepared according to Tomalia and Paige [4]. 2,2′-Bipyrimidine, a commercially available product, was used as purchased. $(CH_3)_2Pt(Me_2SO)_2$, $(CH_3)_4Pt_2(Me_2S)_2$ $(C_6H_5)_2Pt(Me_2SO)_2$ and $(C_6H_5)_2Pt(Me_2S)_2$, used as source of R_2Pt units, were prepared according to the literature methods [5–7].

As a general procedure of synthesis, one mmol of the above thioether or sulphoxide precursors, dissolved in 5 ml of chloroform, was reacted with the stoichiometric quantity of the binucleating ligand bt or bipym. The solution became deep red in a few minutes, and after 30 min the mononuclear complex was precipitated as a red powder using hexane. The yields were almost quantitative, except the recovery loss. Bimetallic derivatives were easily obtained by adding to a chloroform solution of the mononuclear

0020-1693/88/$3.50

complex (one mmol in 5 ml) the stoichiometric amount of mercuric chloride dissolved in the minimum volume of acetone. The deep red solution became immediately yellow and the binuclear compounds were precipitated as yellow powders with hexane. Immediate precipitation occurred for $(C_6H_5)_2Pt(bt)HgCl_2$. Yields were generally good (60% or more).

Analysis.

Dimethylplatinum(II)(2,2'-bithiazoline-N,N'-Pt)

Calc. for $C_8H_{14}N_2PtS_2$: C, 24.55; H, 3.58; N, 7.19. Found: C, 24.12; H, 3.41; N, 6.98%.

Diphenylplatinum(II)(2,2'-bithiazoline-N,N'-Pt)

Calc. for $C_{18}H_{18}N_2PtS_2$: C, 41.45; H, 3.45; N, 5.27. Found: C, 41.49; H, 3.60; N, 5.28%.

Dimethylplatinum(II)(2,2'-bithiazoline-N,N'-Pt-S,S'-Hg)dichloromercury(II)

Calc. for $C_8H_{14}Cl_2HgN_2PtS_2$: C, 14.37; H, 2.09; N, 4.19; S, 9.58. Found: C, 14.21; H, 2.09; N, 4.27; S, 9.90%.

Diphenylplatinum(II)(μ-2,2'-bithiazoline-N,N'-Pt-S,S'-Hg)dichloromercury(II)

Calc. for $C_{18}H_{18}HgN_2PtS_2$: C, 27.27; H, 2.27; N, 3.53; S, 7.99. Found: C, 26.91; H, 2.07; N, 3.50; S, 7.99%.

Dimethylplatinum(II)(μ-2,2'-bipyrimidine)dichloromercury(II)

Calc. for $C_{10}H_{12}Cl_2HgN_4Pt$: C, 18.34; H, 1.83; N, 8.56; Cl, 10.85. Found: C, 18.82; H, 1.89; N, 8.70; Cl, 11.21%.

^1H and ^{13}C NMR spectra were recorded on a WP 80 SY Bruker spectrometer.

Results and Discussion

In the complex $(CH_3)_2Pt(bt)$, the ligand 2,2'-bithiazoline is linked to platinum through nitrogen atoms as in **III**, M = Me_2Pt. This comes from the observation that the –C=N– band, which is in the free ligand at 1600 cm^{-1}, disappears in the above complex, probably buried under the CH_2 bands at *ca.* 1450, probably because double bonds are delocalized in a conjugated system extended from platinum to sulphur atoms. ^1H NMR spectrum of the free ligand, 2,2'-bithiazoline, results in two triplets. Tomalia and Paige [4] assigned the triplet centred at 3.40 ppm to N–CH_2 protons and the one centred at 4.48 ppm to S–CH_2 protons. Such an assignment was judged wrong by Nelson [2a]. The ^{13} C NMR spectrum shows CH_2 signals at δ 33.32 and 65.34. The signals at δ 33.32 is typical of a CH_2 group attached to sulphur, and that at δ 65.34 of a CH_2 group attached to nitrogen in this class of heterocyclic compounds. The protons were assigned by two dimensional $^{13}C\ \{^1H\}$ correlation with those at δ 33.32 and those at δ4.48 attached to the carbon at δ 65.34 (Fig. 1), in agreement with Nelson's assignment.

Coordination to the platinum does not produce noteworthy changes in the chemical shifts and in the coupling constants in the coordinated bithiazoline. In the spectrum of the complex $(CH_3)_2Pt(bt)$ the methylenes still appear as triplets centred at 3.67 (N–CH_2) and 4.63 (S–CH_2) ppm while platinum-bonded methyl groups give rise at 1.23 ppm to a single peak flanked by ^{195}Pt satellites in the expected 1:4:1 intensity ratio ($^2J(^{195}Pt–H)$ = 88.8 Hz). ^1H NMR data rule out the coordination of the ligand through nitrogen and sulphur as in **II**, M = Me_2Pt, since in this latter case four triplets should appear in the spectrum. Moreover, the coordination of the platinum to nitrogen to give **III**, M = Me_2Pt, was confirmed by nuclear Overhauser effect (NOE) difference measurements. Irradiation of the methyl protons at δ 1.23 gave a significant NOE of 1% into the N–CH_2 at δ 4.63 but negligible NOE into the S–CH_2 protons at δ 3.67. This clearly shows that the methyl protons are closer to the N–CH_2 group, than the S–CH_2 group, thus establishing **III**, M = Me_2Pt, as the structure.

The bimetallic complex $(CH_3)_2Pt(bt)HgCl_2$ shows a similar ^1H NMR spectrum. However, while methylene signals were nearly unaffected, the mercuric chloride produces a noteworthy change both in the chemical shift and in the coupling constant of the platinum bonded methyl groups. On the other hand, the presence of ^{195}Pt satellites, together with the lack of ^{199}Hg satellites, rules out the occurrence of oxidative addition of the mercuric chloride to the platinum(II) substrates. Thus, mercury must be

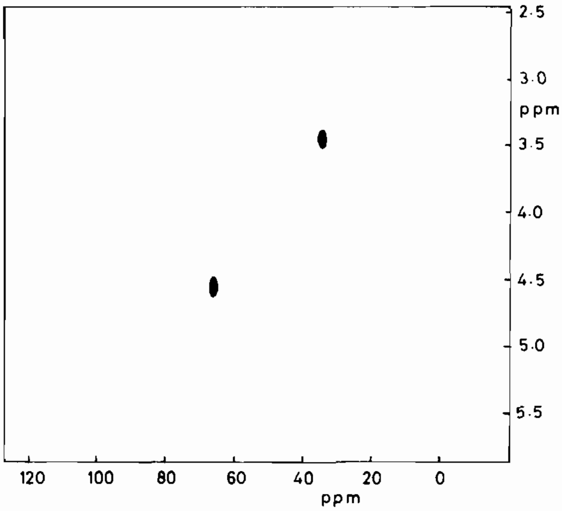
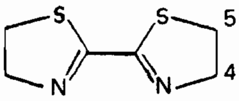
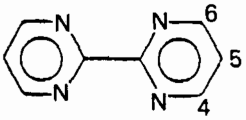


Fig. 1. Two dimensional $^{13}C\{^1H\}$ correlation of 2,2'-bithiazoline.

TABLE I. ^{1}H NMR Data for Mono and Bimetallic Complexes of 2,2'-Bithiazoline and 2,2'-Bipyrimidine

	$\delta(H^5)^a$	$\delta(H^4)^a$	$\delta(H^6)^a$	$\delta(Pt-CH_3)^a$	$^3J(H^4-H^5)$	$^4J(H^4-H^6)$	$^3J(H^5-H^6)$	$^2J(^{195}Pt-H)$
								
2,2'-bithiazoline^b (bt)	3.39(t)	4.48(t)			8.2 Hz			
$(CH_3)_2Pt(bt)^b$	3.67(t)	4.63(t)		1.34	8.2 Hz			88.8 Hz
$(CH_3)_2Pt(bt)HgCl_2{}^b$	3.84(t)	4.57(t)		1.63	8.4 Hz			67.2 Hz
$(C_6H_5)_2Pt(bt)^b$	3.59(t)	4.30(t)			8.3 Hz			
$(C_6H_5)_2Pt(bt)HgCl_2{}^b$	3.75(t)	4.60(broad)			8.2 Hz			
								
2,2'-bipyrimidine^c (bipym)	7.45	9.04	9.04		6.0 Hz		6.0 Hz	
$(CH_3)_2Pt(bipym)$	7.67	9.33	9.49	1.07	5.6 Hz	2.2 Hz	4.8 Hz	87.7 Hz
$(CH_3)_2Pt(bipym)HgCl_2{}^d$	8.22	9.62	9.53	1.83	4.8 Hz	2.2 Hz	5.5 Hz	63.8 Hz

^{a}ppm relative to tms. ^{b}Chloroform d_1. ^{c}Ref. 1c. ^{d}DMF d_7.

located, in the bimetallic complexes, on the sulphur system. The change in chemical shift and in coupling constant can be attributed to a large transmission of electronic effects between the metals through the binucleating ligand.

The methylene signals in the ^{1}H NMR spectra of the compounds $(C_6H_5)_2Pt(bt)$ and $(C_6H_5)_2Pt(bt)HgCl_2$ are not substantially different from those of methyl analogues. However, the triplets centred at 4.30 ppm, in the mononuclear compound, become an unresolved multiplet centred at 4.60 ppm in the bimetallic complex. Signal broadening could be due to the fact that mercuric chloride reaches a rapid equilibrium between the free and coordinated forms

$$(C_6H_5)_2Pt(bt)HgCl_2 \rightleftharpoons (C_6H_5)_2Pt(bt) + HgCl_2$$

According to this, a sharpening of the signal at 4.60 ppm, together with a moderate change in the chemical shift of the broad signals, was obtained in spectra recorded at low temperature.

The proton spectrum of $(CH_3)_2Pt(bipy)$ was reported by Young [1c]. Its bimetallic derivative shows a significant change in the chemical shift and the coupling constant $^2J(^{195}Pt-^1H)$ of the methyl groups, as has been found in $(CH_3)_2Pt(bt)HgCl_2$. Therefore, also in this case, the binucleating bipym acts as a carrier of electrons through the delocalized π orbitals. The hydrogens of coordinated bipym form an ABX system which can be analyzed using iterative computer fitting [8]. The values of coupling constants and chemical shifts, reported in Table I, reproduce unequivocally the observed spectrum.

Eventually, it is necessary to point out the different reactions which occur when mercuric chloride reacts with dimethylplatinum(II)–(α-diimine) complexes on going from bipy and phen to bt and bipym. Kuiper [9] reported that in the reaction of bivalent mercury compounds with $(CH_3)_2Pt(L\text{-}L)$ (L-L = 2,2'-bipyridine, bipy; 1,10-phenanthroline, phen), oxidative addition and/or methyl transfer can occur, depending upon the starting material and the reaction conditions. If bt and bipym are employed, instead of bipy and phen, for the chelating $(CH_3)_2Pt$ unit, a dramatic change in the reaction pattern is observed. In fact, in our case the electrophilic attack of mercuric chloride takes place only on the sulphur atoms system. Analysis of the ^{1}H NMR spectra shows that the resulting bimetallic derivatives do not further react with an excess of mercuric chloride. Hence the coordination of $HgCl_2$ to the free chelating moiety of the mononuclear complexes, makes the d_{z^2} platinum orbital, as well as the platinum–carbon σ-bonds, no more available for the electrophilic attack of mercuric chloride.

References

1 (a) C. Overton and J. A. Connor, *Polyhedron, 1*, 53 (1982); (b) S. Lanza, *Inorg. Chim. Acta, 75*, 131 (1983); (c) V. F. Sutcliffe and G. B. Young, *Polyhedron, 3*, 87 (1984); (d) J. D. Scott and R. J. Puddephatt, *Inorg. Chim. Acta, 89*, L27 (1984); (e) J. D. Scott and R. J. Puddephatt, *Organometallics, 5*, 2522 (1986).

2 (a) J. Nelson, S. M. Nelson and W. D. Perry, *J. Chem. Soc., Dalton Trans.*, 1282 (1976); (b) M. G. B. Drew, T. R. Pearson, B. P. Murphy and S. M. Nelson, *Polyhedron, 2*, 269 (1983).

3 J. C. Huffman and A. P. Sattelberger, *Cryst. Struct. Commun., 10*, 1535 (1981).

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

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

6 J. D. Scott and R. J. Puddephatt, *Organometallics, 2*, 1643 (1983).

7 G. Alibrandi, G. Bruno, S. Lanza, D. Minniti, R. Romeo and M. L. Tobe, *Inorg. Chem., 26*, 185 (1987).

8 Bruker Instruments, Inc., 'Aspect 2000', Software manual, 1982.

9 J. Kuiper, *Inorg. Chem., 17*, 178 (1978).