Formation of Dimethylsulfide Singly-bridged Diplatinum Complexes by Reaction of Bridged Dimers $[Pt_2Cl_4(Pyridine^{subst.})_2]$. Identification of a Labile Diplatinum Precursor with a Single Chloride Bridge

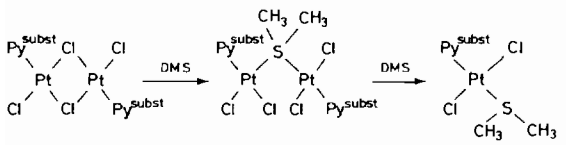
P. COURTOT, R. PICHON, R. RUMIN and J. Y. SALAÜN

Laboratoire de Photochimie, Electrochimie et Chimie Moléculaires de l'Université de Bretagne Occidentale, associé au CNRS (UA 322), 6, Avenue le Gorgeu, 29287 Brest, France

Received March 16, 1985

Amongst the opening reactions by various ligands of diplatinum complexes with chloride bridges $[(PtX_2L)_2]$ studied in our laboratory [1], we obtained complexes with a pyrazine bridge using a bidentate ligand as dimethyl pyrazine [2]. We thought it possible to obtain compounds with a single sulfur bridge using dimethyl sulfide (DMS). We found that DMS is indeed able to open dimers such as $[(PtCl_2Py^{subst.})_2]$ even at low temperature.

The opening of the chloro-bridged complex by DMS occurs according to:



1 2 3

a: $Py^{subst.} = Py^{2,6}; Py^{2,4,6}$
b: $Py^{subst.} = Py^{2}; Py^{4}$
Py^{2}; Py^{4} = 2 or 4-methylpyridine; $Py^{2,6}$ = 2,6-dimethylpyridine; $Py^{2,4,6}$ = 2,4,6-trimethylpyridine.

With crowded pyridines ($Py^{2,6}$ and $Py^{2,4,6}$) the monobridged compound **2a** is rapidly formed (15 min at room temperature, with one or two DMS equivalents) under a *trans, trans* configuration (90%). The *trans* monomer **3a** is formed at R. T. with ten DMS equivalents (24 h, 80% yield) or at 70 °C with two equivalents (24 h, 50% yield).

Compound **3b** with a less crowded pyridine is formed directly (70% yield, 20 °C) with two DMS equivalents as previously reported [1]: *cis* **3b** (30%) and *trans* **3b** (70%), isolated by solid–liquid chromatography.

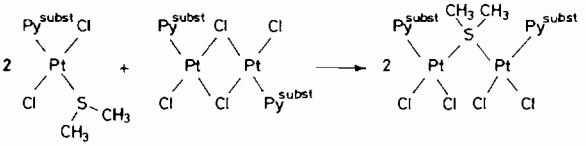
The monobridged compound **2b** can be obtained with a good yield when using one equivalent of DMS at 20 °C (80% yield $Py^{subst.} = Py^{2}$ and 65% $Py^{subst.} = Py^{4}$). This compound is a mixture of three stereoisomers *cis,cis*; *cis,trans* and *trans,trans*, separated at a temperature lower than 10 °C (they interconvert at higher temperature). Their physical characteristics have been determined.

A new type of structure is shown by compounds **3a** ($Py^{subst.} = Py^{2,6}$ and $Py^{2,4,6}$: crowded pyridines) under a unique *trans* stereochemistry, as shown by IR, ^{13}C NMR (terminal DMS at 22.45 ppm) and ^{1}H NMR (J_{Pt-H} = 42 Hz) (Table I). Though doubly bridged thioether complexes of platinum are known [3, 4], only one singly bridged neutral compound is reported [5]. Unfortunately, this compound is very weakly soluble, due to its *cis,cis* configuration, and only IR data were obtained.

Compounds **2** are the first monobridged thioether platinum complexes reported as a mixture of three stereoisomers. These stereoisomers have been separated and identified through IR (ν_{Pt-S} = 405 cm^{-1}), ^{13}C NMR (CH_3 of bridging DMS at 28 ppm) and ^{1}H NMR (J_{Pt-H} = 34 Hz for the *trans* configuration, J_{Pt-H} = 40 Hz for the *cis* configuration).

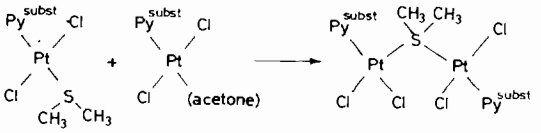
A confirmation of structure **2** is obtained through different syntheses:

(a) Reaction of $[PtCl_2(Py^{subst.})(DMS)]$ with the chlorobridged dimer **1**:



3 1 2

(b) Reaction of $[PtCl_2(Py^{subst.})(DMS)]$ with *trans* $[PtCl_2(Py^{subst.})(acetone)]$ [6] at 0 °C, yielding only *cis,trans* and *trans,trans* **2**:



3 2

Concerning the splitting of dichloro bridged diplatinum compounds, it has generally been assumed [7] that the initial ligand attack is slow, followed by a rapid second step. We have recently shown [2] that such a mechanism was not operative in the case of pyrazine opening of **1**, which yields a singly bridged complex (rapid first step). We have observed a new example with the reaction of one DMS equivalent on dimer **1** ($Py^{subst.} = Py^{2}$) at −40 °C: a new monochlorobridged complex is formed under these conditions. This new compound **4**, which is stable only

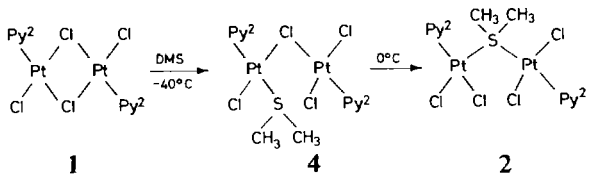
0020-1693/85/$3.30 © Elsevier Sequoia/Printed in Switzerland

TABLE I. Main Physical Constants of Complexes **2**, **3** and **4**.

Substituted pyridine	^{1}H NMR, ppm			^{13}C NMR, ppm			IR cm^{-1}		F °C
	CH_3 pyridine(2,6)	CH_3 pyridine(4)	CH_3(sulfide)	CCH_3 pyridine(2,6)	CCH_3 pyridine(4)	CCH_3 sulfide	ν_{Pt-S}	ν_{Pt-Cl}	
Complexes **2**									
$Py^{2,4,6}$ (*trans, trans*)	3.23 J_{Pt-H} = 14 Hz	2.31	3.14 J_{Pt-H} = 34 Hz	26.74 J_{Pt-C} = 28 Hz	20.74	27.53	405	350	216
$Py^{2,6}$ (*trans, trans*)	3.32 J_{Pt-H} = 14 Hz		3.18 J_{Pt-H} = 35 Hz	27 J_{Pt-C} = 27 Hz		28	405	340	234
Py^2 (*cis, cis*)	[a]			[a]			415	320 335	205
Py^2 (*cis, trans*)	2.73 J_{Pt-H} = 12 Hz		3.36 J_{Pt-H} = 40 Hz	27.89 J_{Pt-C}		29.54	405	345	194
	3.27 J_{Pt-H} not determined		3.42 J_{Pt-H} = 32 Hz	26.31 J_{Pt-C} not determined		29.42		330sh	
Py^2 (*trans, trans*)	3.21 J_{Pt-H} = 13 Hz		3.17 J_{Pt-H} = 35 Hz	26.25 J_{Pt-C} = 29 Hz		27.47	410	340	189
Py^4 (*cis, cis*)	[a]			[a]			425	315 340	210
Py^4 (*cis, trans*)		2.39 2.37	3.26 J_{Pt-H} = 32 Hz J_{Pt-H} = 41 Hz		21.68	29.73	405	325sh 340	200
Py^4 (*trans, trans*)		2.44	3.23 J_{Pt-H} = 33 Hz		21.32	28.63	405	342	205
Complexes **3**									
$Py^{2,4,6}$ *trans*	3.19 J_{Pt-H} = 13 Hz	2.31	2.41 J_{Pt-H} = 42 Hz	26.61 J_{Pt-C} = 26 Hz	20.71	22.45 J_{Pt-C} = 14.5 Hz	330	355	165
$Py^{2,6}$ *trans*	3.25 J_{Pt-H} = 13 Hz		2.42 J_{Pt-H} = 42.3 Hz	26.92 J_{Pt-C} = 26 Hz		22.47 J_{Pt-C} = 13.7 Hz	325sh	335	135
Complex **4**									
Py^2	3.33 J_{Pt-H} = 12 Hz		2.62 J_{Pt-H} = 44 Hz	27.29		22.78			
	3.01 J_{Pt-H} = 13 Hz		2.40 J_{Pt-H} = 44 Hz	26.85		22.29			

[a]Compounds too weakly soluble.

at low temperature, is transformed into complex 2 within 15 min at 0 °C:



1 **4** **2**

Two methyl signals characteristic of terminal DMS and two methyl signals for 2-methylpyridines in different environments are found for **4** in ^{1}H and ^{13}C NMR (Table I). Such a structure **4** (two or three isomers) with only one bridging chloride is therefore a highly probable intermediate for the formation of the DMS monobridged complex 2.

In conclusion, we have been able to isolate at low temperature the three isomers of the DMS monobridged diplatinum complexes **2a** (Py^2; Py^4). With crowded substituted pyridines ($Py^{2,6}$; $Py^{2,4,6}$) the *trans,trans* compounds **2b** are stable at room temperature but the DMS monomers **3b** can be obtained under different conditions.

References

1 P. Courtot, R. Rumin, A. Peron and J. P. Girault, *J. Organomet. Chem., 145,* 343 (1978).
2 R. Pichon, R. Rumin and J. Y. Salaün, *J. Organomet. Chem.,* in press.
3 S. G. Murray and F. R. Hartley, *Chem. Rev., 81,* 365 (1981).
4 J. D. Scott and R. J. Puddephatt, *Organometallics, 2,* 1643 (1983).
5 P. L. Goggin, R. J. Goodfellow and F. J. S. Reed, *J. Chem. Soc., Dalton Trans.,* 576 (1974) and ref. cited therein.
6 J. Auffret, P. Courtot, R. Pichon and J. Y. Salaün, *J. Organomet. Chem., 262,* C19 (1984).
7 G. K. Anderson and R. J. Cross, *Chem. Soc. Rev., 9,* 185 (1980).