

NOTE

Halogen Scrambling in Pt(II) Substitution Reaction

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Addition of NBu_4Br to $\text{M}[\text{PtCl}_3(\text{PPh}_3)]$ in dichloromethane results in a redistribution of halogens and formation of all six isomers of the type $\text{M}[\text{PtBr}_{3-x}\text{Cl}_x(\text{PPh}_3)]$, ($x = 0, 1, 2$ and 3), which have been identified by ^{31}P - $\{^1\text{H}\}$ NMR spectroscopy.

Oxidative-addition of bromine to square-planar *trans*-dichloro platinum(II) complexes was found to result in a statistical scrambling of chlorine/bromine and formation of the octahedral platinum(IV) complexes, *trans*- $[\text{PtCl}_{4-x}\text{Br}_x(\text{PR}_3)_2\text{L}]$ $\text{R} = \text{Et}, \text{Bu}, \text{L} = \text{PEt}_3, \text{Py}, \text{O-substituted Py}$ ($\text{Py} = \text{pyridine}$)¹, and a related redistribution occur during oxidative addition of gold(I) complexes. Similar results have been obtained for chlorine/bromine scrambling in $[\text{PtX}_3\text{L}]$ ($\text{X} = \text{halogen}, \text{L} = \text{phosphine ligand}$) complexes^{2,3,4}.

We have recently shown that statistical redistribution of chlorine/bromine occurs on addition of chlorine (excess mol) to $[\text{PtCl}_3(\text{PF}_3)]^-$ (1 mol) in chloroform solution at 25°C .⁵ The present work reports that similar results are obtained on addition of bromine (7 mol) to $[\text{PtCl}_3(\text{PPh}_3)]$ (1 mol) in the same condition.

The ^{31}P NMR spectrum was obtained on jeol FT FX NMR 90 Q spectrophotometer for solution of complexes in deuterio dichloromethane; chemical shifts (high frequency is positive) are quoted relative to external 85% H_3PO_4 . The value of δ_p was obtained with solutions containing 100 mg of the complex. The preparation of $(\text{NBu}_4)[\text{PtCl}_3(\text{PPh}_3)]$ was carried out exactly as described^{5,6} and analyses agree with those previously found. The preparation of $(\text{NBu}_4)[\text{PtBr}_{3-x}\text{Cl}_x(\text{PPh}_3)]$ ($x = 0, 1, 2$ and 3) was carried out by adding NBu_4Br (excess mol) to a solution of $(\text{NBu}_4)[\text{PtCl}_3(\text{PPh}_3)]$ (1 mol) in dichloromethane at 25°C .

Addition of bromide (excess mol) to $(\text{NBu}_4)[\text{PtCl}_3(\text{PPh}_3)]$ (1 mol) at room temperature in dichloromethane results in the formation of all six isomers of the type $(\text{NBu}_4)[\text{PtBr}_{3-x}\text{Cl}_x(\text{PPh}_3)]$ ($x = 0, 1, 2$ and 3) (See Fig. 1).

The ^{31}P - $\{^1\text{H}\}$ NMR spectra of the solution show all six isomers to be present and (neglecting satellites due to ^{195}Pt -coupling) consists of six lines. Thus the two sets of resonances are due to either chlorine or bromine being *trans* to phosphine and the three resonances within each set are due to progressive replacement of chlorine *cis* to the phosphine by bromide (see Table). Their assignment follows from a comparison with the spectra of authentic $(\text{NBu}_4)[\text{PtX}_3(\text{PPh}_3)]$ ($\text{X} = \text{Cl}^-$ or

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TABLE-1
 CHEMICAL SHIFTS (ppm) AND COUPLING CONSTANTS (Hz) FOR COMPLEXES OF THE TYPE
 $[\text{PtBr}_{3-x}\text{Cl}_x(\text{PPh}_3)]$ (X = 0, 1, 2 and 3)

Isomers								
δ (p.p.m)	4.463	4.297	3.752	2.722	2.462	2.389		
$^1J_{(Pt-P)}$	4092.39	3878.23	4006.13	3900.72	3752.92	3830.50		
Intensity:								
Predicted	1	2	1	2	1	1		
Found	1.3	1.9	1	2.1	1.1	0.75		

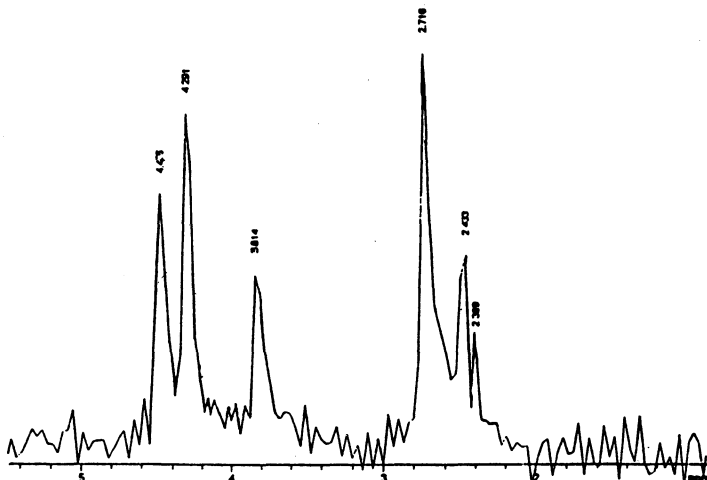


Fig. 1 $^{31}\text{P}\{-^1\text{H}\}$ NMR spectrum of $[\text{PtBr}_{3-x}\text{Cl}_x(\text{PPh}_3)]$ ($X = 1, 2$ and 3).
Isomer numbers refer to Scheme and Table

Br^-) and from the almost systematic upfield shift of δ_{P} and decrease in $^1J_{(\text{Pt}-\text{P})}$ found on progressive replacement of chlorine or bromine *cis* to the phosphine in *trans*- $[\text{PtBr}_x\text{Cl}_{4-x}(\text{PEt}_3)\text{L}]$,¹ and similar complexes^{2, 6, 7}

There is a good correlation between the total electronegativity of the halides present in these complexes which is in good agreement with literature^{2, 3, 5} and depend only slightly on whether the chloride is *cis* or *trans* to phosphine.

ACKNOWLEDGEMENT

We are most grateful to the university of Bu-Ali-Sina for a grant and Mr. M. Zebardjadian for plotting NMR spectra and Mrs. moosavei for typing.

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(Received: 6 September 1999; Accepted: 14 December 1999)

AJC-1955