SHORT PAPER

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Halogen scrambling in Pt(II) substitution reactions; a ^{31}P NMR study[†]

S. J. Sabounchei* and V. Jodaien

Department of Chemistry, Bu-Ali Sina University , Zip Code 65174, Hamadan , Iran

Addition of NBu_4Br to M[$PtCl_3\{P(C_6H_5Me-4)_3\}$] in dichloromethane results in a redistribiution of halogens and formation of all six isomers of the type M[$PtBr_{3}$-xClx$\{P(C_6H_5Me-4)_3\}$],(x = 0,1,2 and 3), which have been identified by ^{31}P–{^1H}NMR spectroscopy.

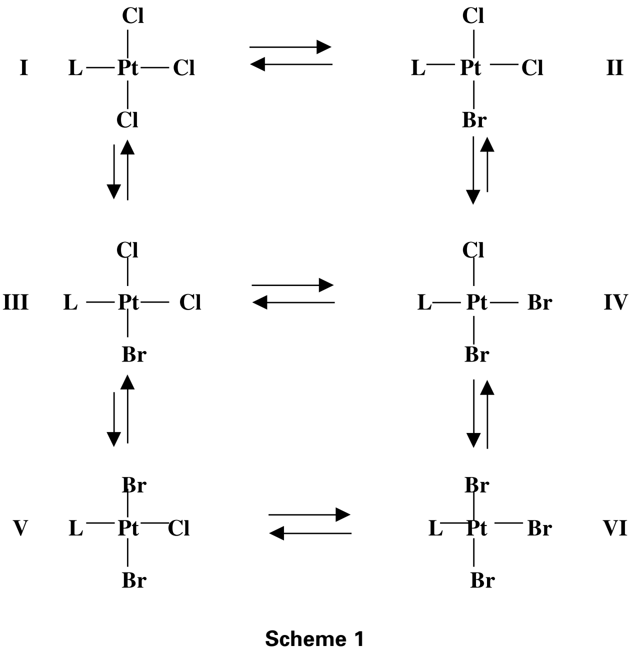
Keywords: Pt (II) substitution, scrambling

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*-[$PtCl_{4-x}Br_x(PR_3)L$], [R=Et, Bu; L=PEt_3, Py, O-substituted Py (Py=pyridine)][1]. A related redistribution occurs during oxidative addition of gold (I) complexes.[2] Similar results have been obtained for chlorine/bromine scrambling in [PtX_3L] (X=halogen, L=phosphine ligand) complexes[3,4] and we have recently shown that statistical redistribution of chloride/ bromide occurs on addition of chloride and bromide (excess) to $[PtCl_3(PF_3)]^-$ and $[PtCl_3(PPh_3)]^-$ (1 mol) respectively in chloroform at 25°C.[5,6]

The present work reports that similar results are obtained on addition of bromide (excess) to [$PtCl_3\{P(C_6H_5Me-4)_3\}$] (1 mol) under the same conditions.

The $^{31}P\{^1H\}$ NMR spectra was obtained on a Jeol FX-90Q spectrophotometer for solutions of complexes in deuterio dichloro methane; chemical shifts are quoted relative to external 85% H_3PO_4.

The value of δp was obtained with a solution containing 60 mg of the complex. The preparation of (NBu_4) [$PtCl_3\{P(C_6H_5Me-4)_3\}$] was carried out as described in the literature and analyses agree with those previously found.[7]



Scheme 1

Addition of bromide (3 mol) to (NBu_4) [$PtCl_3\{P(C_6H_5Me-4)_3\}$]. (1 mol) at room temperature in dichloromethane results in the bromination of all six isomers of the type (NBu_4)[$PtBr_{3-x}Cl_x\{P(C_6H_5Me-4)_3\}$] (x = 0,1,2 and 3) (Scheme 1).

The $^{31}P\{^1H\}$NMR spectra of the solution show all six isomers to be present and satellites to consist of six lines. By comparison of these spectra with those of [$PtCl_{3-x}Br_x(PPh_3)$], we suggest that, two types of (IV) and (V) isomers, in solution, appear at the same frequency and show coupling constants with only a small differences. On the other hand, the intensities of these lines are in good agreement with the intensity of six expected isomers (Fig.1).

Thus, these two sets of resonances are due to either chloride or bromide being *trans* to phosphine and the three resonances within each set are due to progressive replacement of chloride *cis* to the phosphine by bromide (see Table 1).

Their assignment follows from a comparision with the spectra of authentic (NBu_4)[$PtX_3\{P(C_6H_5Me-4)_3\}$]) (X = Cl^- or Br^-) and from the almost systematic upfield shift of δp and decrease in $J_{(Pt\text{-}P)}$ found on progressive replacement of chlorine or bromine *cis* to the phosphine in *trans*- [$PtBr_XCl_{4-X}(PEt_3)L$] (X = 0,...,4), and similar complexes.[8] There is a good correlation between the total electronegativity of the halides present in these complexes which is in good agreement with the literature[2,4] and depends only slightly on whether the chloride *cis* or *trans* to phosphine.

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References

1 B.T. Heaton and K.J. Timmines, *Chem. Comm.*, 1973, 931
2 B.T. Heaton and R.J. Kelsey, *Inorg. Nucl. Chem. Lett.* 1975, **11**, 363
3 B.T. Heaton and R.J. Foot Ph. D. Thesis, University of Kent, 1976
4 S. Ahrland, J. Chatt and N.R. Davies, *Quart.Rev.*, 1958, **12**, 256
5 S.J. Sabounchei and M.H. Sadre, *Orient. J. Chem.*, 1999, **15**, 49
6 S.J. Sabounchei and H. Khavasei, *Asian J. Chem.*, 2000, **12**, 2, 587
7 C. Brown, B.T. Heaton and S.J. Sabounchei, *J. Organomet. Chem.*, 1977, **142**, 413
8 D.W.W. Anderson, E.A.V. Absworth and D.W. Rankin, *J.C.S. Dalton*, 1973, 854

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* To receive any correspondence. E-Mail: Jsabounchei@ yahoo.co.uk

[†] This is a Short Paper, there is therefore no corresponding material in *J Chem. Research (M).*

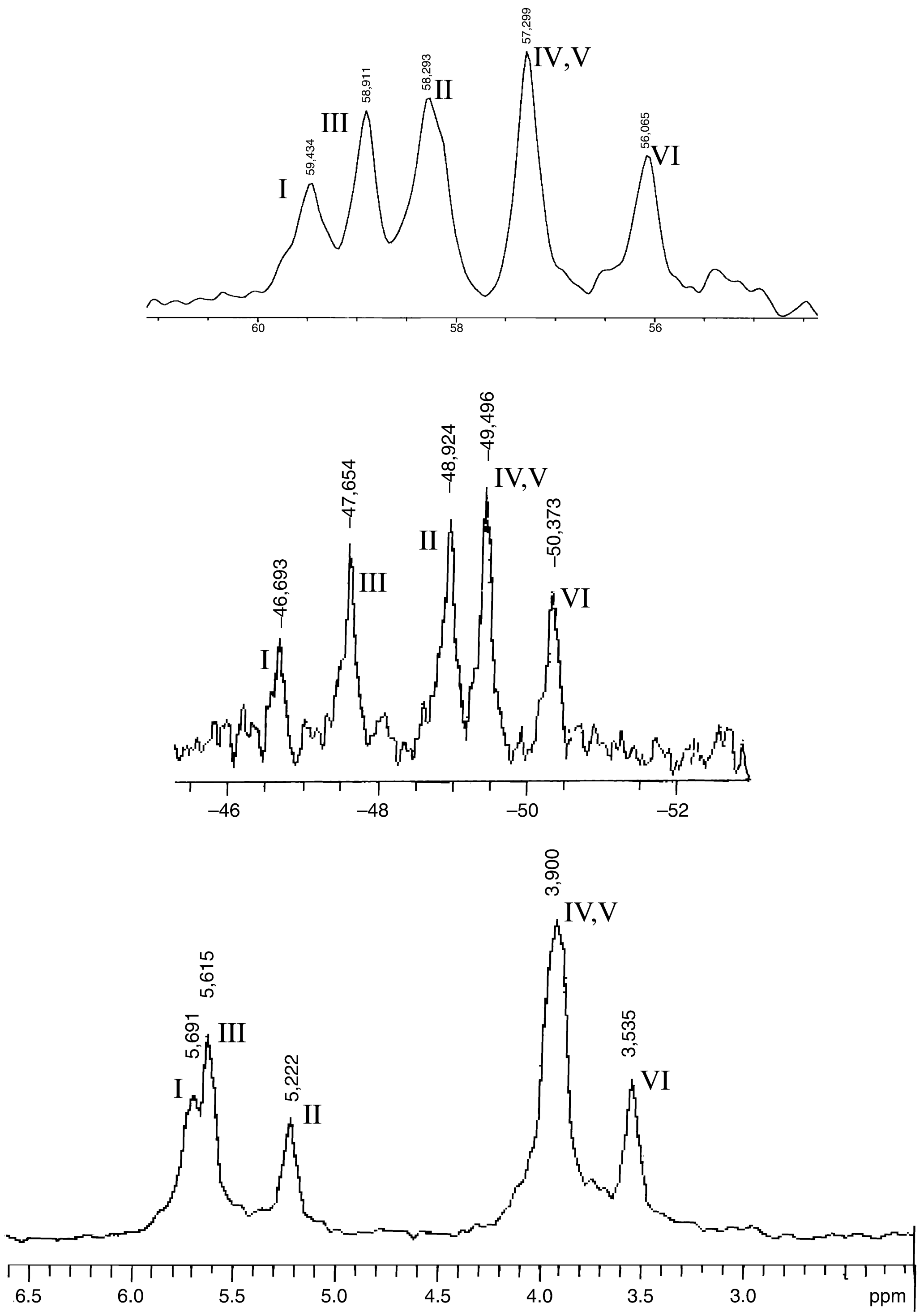
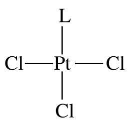
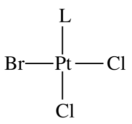
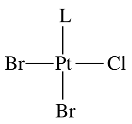
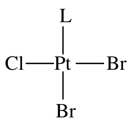
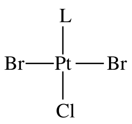
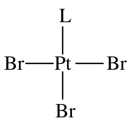


Fig. 1 ^{31}P-{^{1}H}NMR spectra of [$PtBr_{3-X}Cl_X$ {$P(C_6H_5Me-4)_3$}] (X = 0,1,2 and 3). Isomer numbers refer to Scheme 1 and Table 1.

Table 1 Chemical shift (ppm) and coupling constant (Hz) for complexes of the type [$PtBr_{3-x}Cl_x${$P(C_6H_5Me-4)_3$}](x = 0,..., 3)

Isomers	 $\mathrm{Cl{-}\overset{L}{\underset{Cl}{Pt}}{-}Cl}$ I	 $\mathrm{Br{-}\overset{L}{\underset{Cl}{Pt}}{-}Cl}$ III	 $\mathrm{Br{-}\overset{L}{\underset{Br}{Pt}}{-}Cl}$ II	 $\mathrm{Cl{-}\overset{L}{\underset{Br}{Pt}}{-}Br}$ IV	 $\mathrm{Br{-}\overset{L}{\underset{Cl}{Pt}}{-}Br}$ V	 $\mathrm{Br{-}\overset{L}{\underset{Br}{Pt}}{-}Br}$ VI
δ(ppm)	5.691	5.615	5.222	3.900		3.536
$^1J_{(Pt-P)}$	3897.4	3862.6	3887.8	3872.6		3859.7
Intensity predicted	1	2	1	2	1	1
Intensity found	0.92	1.88	0.92	2.94		1.1