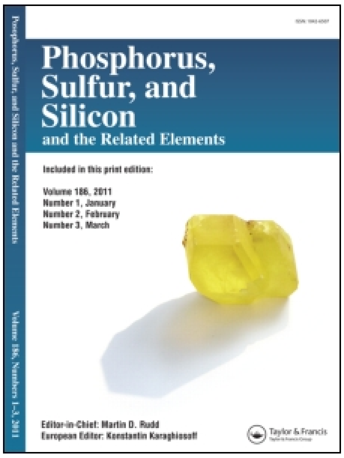

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A ^{31}P NMR STUDY OF TERTIARY PHOSPHINE COMPLEXES OF PLATINUM(II) AND PALLADIUM(II)

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A ^{31}P NMR STUDY OF TERTIARY PHOSPHINE COMPLEXES OF PLATINUM(II) AND PALLADIUM(II)

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Complexes of the type $(NBu_4)[MCl_3(PR_3)]$*(R = P.Tolyl,Ph,Bu) (M = Pt, Pd) are prepared by the reaction of* MCl_2 *or* $K_2[MCl_4]$ *by phosphine ligands. Addition of* NBu_4Br *or* NBu_4I *to these compounds, in dichloromethane results in a redistribution of halogens and formation of all six isomers of the type* $[MBr_{3-X}Cl_X(PR_3)]$ *(X = 0, 1, 2, and 3) which have been identified by* ^{31}P*-*$\{^1H\}$ *NMR spectroscopy. The intensities show that the products are proportional to the statistical distribution.*

Keywords: Pd(II); Pt(II); scrambling; triphenylphosphine; tributylphosphine; triparatolylphosphine

Oxidative-addition of bromide to square-planer trans-dichloro platinum (II) complexes was found to result in a statistical scrambling of chloride/bromide 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] Related redistribution occurs during an 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] We have recently shown that statistical redistribution of chloride/bromide occurs on addition of chloride and bromide (3 mmol) to $[PtCl_3(PF_3)]^-$ and $[PtCl_3(PPh_3)]^-$ (1 mol) in chloroform at 25°C respectively.[5–7] The present work reports similar results on addition of halide in excess mol (3:1) to $(NBu_4)[MCl_3(PR_3)]$(M = Pd, Pt, R = Bu, p.Tolyl, Phenyl). The products are six isomers of the type $(NBu_4)[MBr_XCl_{3-X}(PR_3)]$.

We are most grateful to the University of Bu-Ali Sina for a grant and Mr. M. Zebarjadian for plotting the NMR spectra.

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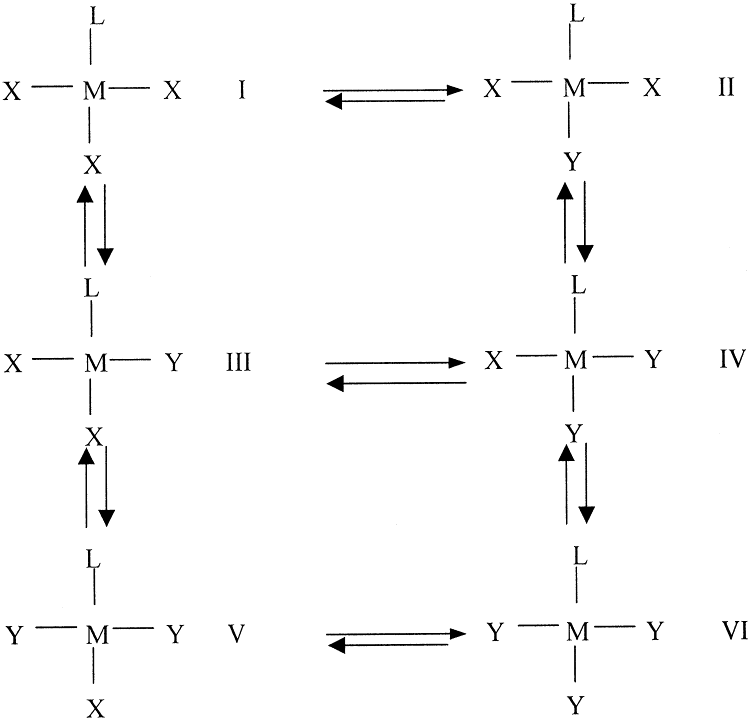
RESULTS AND DISCUSSION

Addition of halide (3 mmol) to $(NBu_4)[MCl_3(PR_3)]$(1 mmol) at room temperature in dichloromethane results in the preparation of all six isomers of the type $(NBu_4)[MCl_{3-x}Y_x(PR_3)]$(Y = Br, I; x = 0, 1, 2, and 3) (Scheme 1).



SCHEME 1

The intensity of each isomer, according to the statistical distribution, would be:

$$\begin{array}{cc} \text{I:III:V} & \text{II:IV:VI} \\ \downarrow & \downarrow \\ 1{:}2{:}1 & 1{:}2{:}1 \end{array}$$

The $^{31}P\{^1H\}$ NMR spectra of the solutions resulting from the above reactions in complexes $[PtCl_{3-x}Br_x(PBu_3)]^-$ (x = 0, . . . , 3), show all six isomers to be present and (neglecting satellites due to ^{195}Pt-coupling) consist of two sets of three almost equally spaced lines. Thus the two

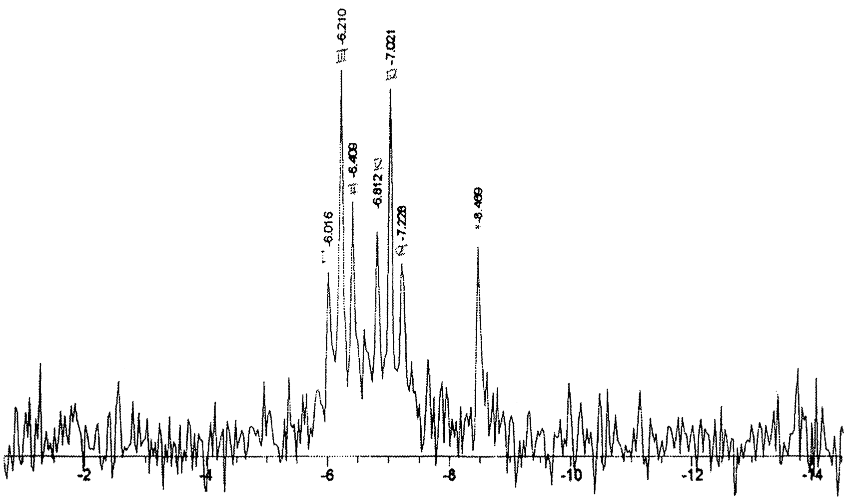


FIGURE 1 $^{31}P\{^1H\}$NMR spectra of $[PtCl_{3-x}\,Br_x\,(PBu_3)]^-$ ($x = 0, \ldots, 3$) (satellites have been omitted for clarity and the line at −8.489 is due to impurity).

sets of resonances in the spectra of are assigned to isomers with either chlorine or bromine trans to phosphine and the three resonances within each set are due to progressive replacement of chloride by bromide cis to the phosphine ligand (Figure 1 and Table I).

There is a good correlation between the total electronegativity of the halides present in these complexes and δ_p, which is in good agreement with the literature[2,4] and depends only slightly on whether the chloride cis or trans to phosphine.

Addition of iodide (3 mmol) to (NBu_4) $[PtCl_3\,(PBu_3)]$ (1 mmol) at room temperature in dichloromethane produces isomers of the type (NBu_4) $[PtCl_{3-x}\,I_x\,(PBu_3)]$ ($x = 0, \ldots, 3$) which have been identified by ^{31}P NMR spectroscopy. By comparison of these spectra with those of $[PtBr_x\,Cl_{3-x}\,(PBu_3)]^-$, we suggest that, two types of (I), (III); (II), (IV) and (V), (VI) isomers appear, in solution, at three frequencies (Figure 2 and Table II).

TABLE I Chemical Shift (ppm) for Complexes of the Type $[Pt\,Br_x\,Cl_{3-x}\,(PBu_3)]^-$ ($x = 0, \ldots, 3$)

Isomers	I	III	II	V	IV	VI
δ(ppm)	−6.01	−6.21	−6.40	−6.81	−7.02	−7.28
Intensity found	1	1.92	1.06	1	1.76	0.9
Intensity predicted	1	2	1	1	2	1

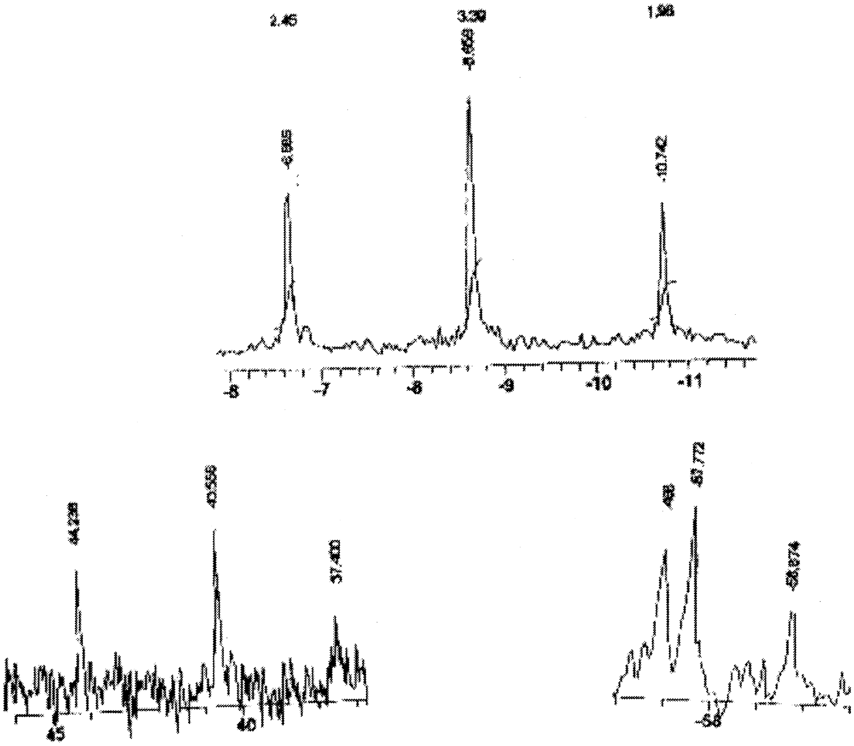


FIGURE 2 $^{31}P\{^1H\}$ NMR spectra of $[PtCl_{3-x} I_x (PBu_3)]^-$ (x = 0, . . . , 3).

Their assignment follows from a comparison with the spectra of authentic (NBu_4) $[PtCl_3 (PBu_3)]$ and from the almost systematic upfield shift of δ_p and decrease in $J_{(Pt-P)}$ found on progressive replacement of chlorine or bromine cis to the phosphine in trans-$[PtBr_x Cl_{3-x} (PEt_3)L]$ (x = 0, . . . , 3) and similar complexes.[11,12]

Addition of iodide (3 mmol) to (NBu_4) $[PdCl_3 (PPh_3)]$ (1 mmol) at room temperature in dichloromethane results halide scrambling with

TABLE II Chemical Shift (ppm) and Coupling Constant (Hz) for Complexes of the Type $[PtCl_{3-x} I_x (PBu_3)]^-$ (x = 0, . . . , 3)

Isomers	I and III	II and IV	V and VI
δ(ppm)	−6.68	−8.65	−10.74
$^1J_{(Pt-P)}$ (Hz)	3685.7	3564.1	3492.0
Intensity found	2.45	3.39	1.98
Intensity predicted	1 + 2	1 + 2	1 + 1

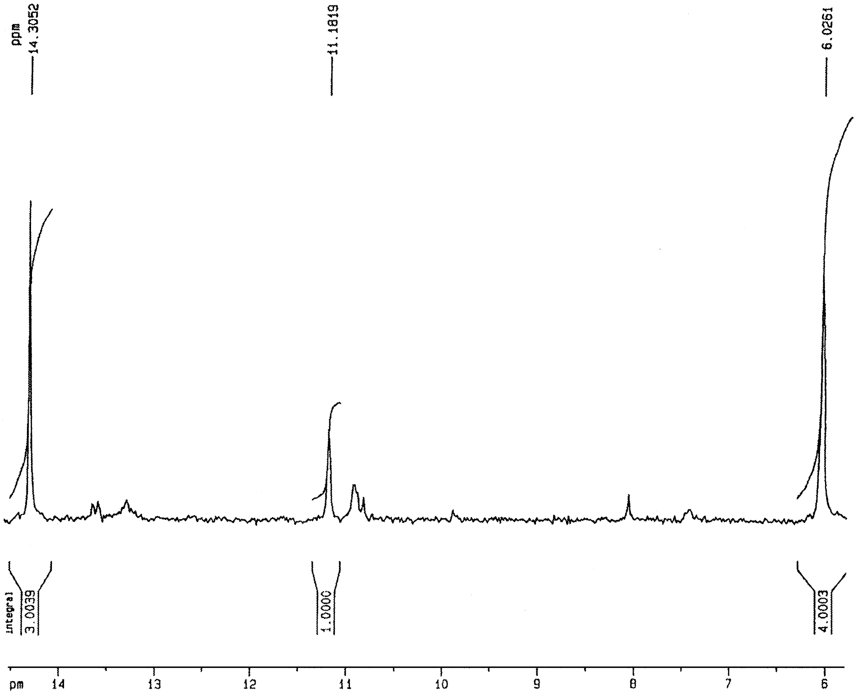


FIGURE 3 $^{31}P\{^1H\}$ NMR spectra of $[PdCl_{3-x}\,I_x\,(PPh_3)]^-$ (x = 0,…, 3).

formula of $(NBu_4)[PdCl_{3-x}I_x(PPh_3)](x = 0,\ldots, 3)$ which identified by ^{31}P NMR spectroscopy. The six isomers appear at three frequencies, which we suggest two types of (I) and (III), three types of (V), (IV), and (VI) appear at the same frequency (Figure 3 and Table III).

Finally, in $(NBu_4)[PdCl_{3-x}Br_x(P.Tolyl)](x = 0,\ldots, 3)$ the halogen scrambling show six isomers where two type of (I) and (V) have chemical shifts in 304.22 ppm and two others (III) and (V) are placed in 306.56 ppm. On the other hand, intensities of these peaks are in good agreement with the intensity of scrambling that we had expected (Figure 4 and Table IV).

TABLE III Chemical Shift (ppm) for Complex of the Type $[PdCl_{3-x}\,I_x\,(PPh_3)]^-$ (x = 0,…, 3)

Isomers	I and III	II	IV and V and VI
δ (ppm)	14.3	11.18	6.02
Intensity found	3	1	4
Intensity predicted	1 + 2	1	2 + 1 + 1

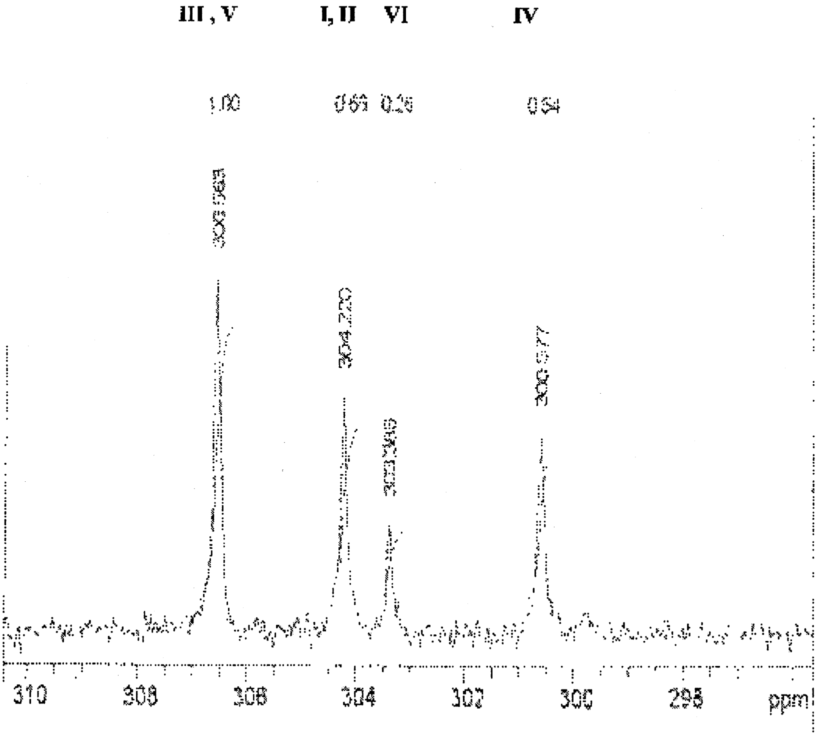


FIGURE 4 $^{31}P\{^{1}H\}$ NMR spectra of $[PdCl_{3-x}Br_x(P(P.Tolyl)_3)]$ (x = 0, ..., 3).

As a result, the intensities of all the complexes in these lines are in good agreement with the intensity of six expected isomers.

EXPERIMENTAL DETAIL

Preparation of cis-$[MCl_2(PR_3)_2]$

Distilled water (5 ml) and ethanol (95%, 2 ml) were mixed in a Schlenk tube and degassed three times by vacuum pump. When the contents

TABLE IV Chemical Shift (ppm) for Complexes of the Type $[Pd\,Br_x\,Cl_{3-x}\,(P(P.Tolyl)_3)]^-$ (x = 0, ..., 3)

Isomers	I, II	III, V	IV	VI
δ (ppm)	304.22	306.56	300.57	303.38
Intensity found	0.66	1	0.54	0.26
Intensity predicted	2	3	2	1

were returned to room temperature the Schlenk tube was flooded with nitrogen gas.

Solid potassium tetrachloropalladate(II) or platinate(II) (0.5 g, 2.4 mmol) was added with a small stir bar and stirred until the solid had dissolved. Tertiary phosphine (4.8 mmol) was added under nitrogen by syringe to the reaction vessel. The contents of the Schlenk tube were stirred vigorously overnight at about 25°C. The stirring was sufficiently vigorous to prevent the phosphine from layering on the surface of the reaction mixture.

The product may contain small amounts of trans isomer mixed with the desired cis-$[MCl_2(PR_3)_2]$. Although such an impurity does not affect the synthesis of the dimer $[M_2Cl_4(PR_3)_2]$, conversion of the trans to the cis can be achieved by suspending the dry solid in pentane under nitrogen and adding two drops of the corresponding tertiary phosphine, stirring until the color is lost. The less soluble cis isomer may be filtered off and dried under vacuum.

The solution was concentrated in vacuum to remove most of the ethanol, and the white precipitate was allowed to settle. The supernatant was decanted under a nitrogen atmosphere, and the remaining solid was dried in vacuum. Once the free phosphine had been removed the product was totally air-stable even in solution. Purity and characterization was established by ^{31}P NMR spectroscopy (dichloromethane or chloroform were suitable solvents). All ^{31}P NMR samples were prepared by evaporation of the solvent.[8]

^{195}Pt ($I = 1/2$) is only 33.8% naturally abundant, all resonances in Pt complexes are giving rise to a symmetrical "triplet" of relative intensities 1:4:1, due to coupling between ^{195}Pt and ^{31}P. In palladium complexes ($I = 0$), synthesis can be established by comparing the chemical shift of the first complexes and the final product.

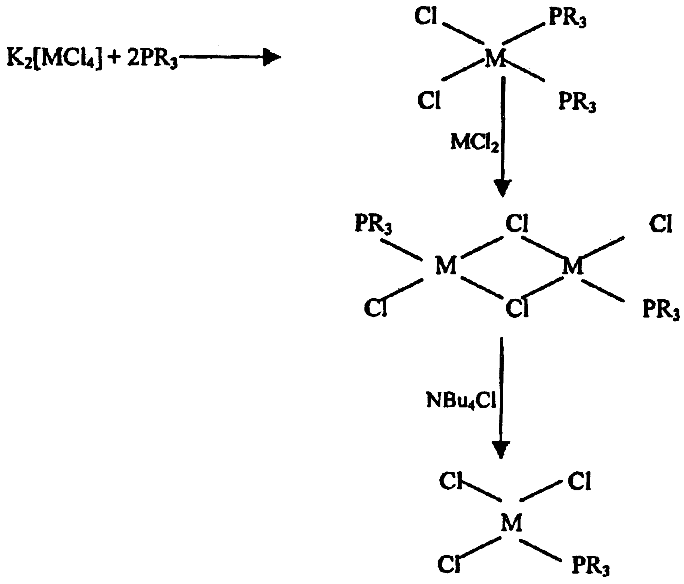
Preparation of $[M_2Cl_4(PR_3)_2]$

Binuclear compounds of M(II) by the type $[M_2Cl_4(PR_3)]$ are useful intermediates for preparation of complexes containing mixed ligands. In a review[9] of the methods available and their limitation, the most useful method recommended for the preparation of complexes where the uncharged ligand is a tertiary phosphine, consisted in melting together the mononuclear complexes $[MCl_2(PR_3)]$ with MCl_2 (1:1). The success of this method depends on the mixture's remaining in the molten state until reaction is complete. It is therefore necessary to work at high temperatures when preparing high-melting compounds. This is not always possible as high temperatures cause excessive decomposition of the products. Some of the complexes decompose before melting. Thus by using a slurry of the reactants in a high-melting hydrocarbon solvent, we can overcome these difficulties. The hydrocarbon assists the reaction by keeping the reagents mobile, by lowering their melting points and by dissolving them to a slight extent. The hydrocarbon is selected so that it refluxes at the required reaction temperature, and the insoluble reaction products are obtained by extracting the diluent with light petroleum or diethyl ether.

In these works the naphthalene in platinum and p.xylene in palladium added to mixture (10 cc of hydrocarbon for 2–3 g of reactants), then heated in an oil-bath at the required temperature with occasional stirring. The product is then extracted with dichloromethane and recrystallised from the solvent.[9]

Preparation of $[MCl_3(PR_3)]^-$

Treatment of dimer with NBu_4I or NBu_4Br, stirring an hour in dichloromethane, results in bridge cleavage and the complexes of $[MCl_3(PR_3)]$ are produced.[10] The product is then filtered off to remove unreacted molecules and recrystallised from dichloromethane. A three-step synthesis of a complex phosphine platinum (II) or palladium species is described below:



Preparation of [MCl$_{3-x}$Y$_x$(PR$_3$)]

The preparation of [MCl$_{3-x}$ Y$_x$(PR$_3$)] (Y = 0, 1, 2, and 3) was carried out by adding NBu$_4$Br or NBu$_4$I (1, 2, 3, and excess mmol) to solution of [MCl$_3$(PR$_3$)]$^-$ (1 mmol) in dichloromethane at 25°C.

All the ^{31}P{^{1}H} NMR spectra was obtained on Jeol FX-90Q spectrophotometer for solution of complexes in deutrio dichloro methane; chemical shifts are quoted relative to external 85% H$_3$PO$_4$. The value of δp was obtained with solution containing 60 mg of the complex.

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