New [PtCl(monophosphine)(chiral bisphosphine)]⁺ cations

László Kollár [*,a] and Gábor Szalontai [b]

[a] *Institute of Organic Chemistry, University of Veszprém and* [b] *Central Laboratory, University of Veszprém,*
*P.O. Box 158, H-8201 Veszprém (Hungary)*

Abstract

[PtCl(P)(P–P)]⁺ cations (P monodentate, P–P bidentate tertiary phosphines) have been derived quantitatively from PtCl₂(P–P) and monophosphines in the presence of SnCl₂, and characterised by ³¹P NMR spectroscopy and conductivity measurements.

Introduction

The formation of $[PtXP_3]^+$ cationic species has been known for many years [1] (eq. 1):

$$PtCl(X)P_2 + P + NaClO_4 \rightarrow \left[Pt(X)P_3\right]^+ \left[ClO_4\right]^- + NaCl \qquad (1)$$
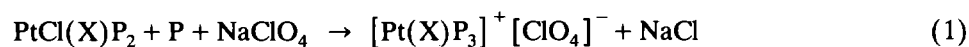
(X = H, R; P = monophosphine)

If the sodium ion is not present to remove the chloride as a precipitate the equilibrium lies far to the left.

In this paper we describe the quantitative formation of [PtCl(monophosphine)(chiral bisphosphine)]⁺ cations and their characterisation by NMR spectroscopy. This work was prompted by the observation of a significant increase in the optical yield in platinum-catalysed enantioselective hydroformylation when a monophosphine–chiral bisphosphine "mixed system" was used in the presence of SnCl₂ [2]. The same effect was noted previously in the palladium-catalysed carbonylation [3], and marked effects were also detected in rhodium-catalysed asymmetric hydrogenation reaction [4].

Results and discussion

Addition of monodentate phosphines (P) of various compositions to a solution of PtCl₂(P–P) resulted in formation of the [PtClP(P–P)]⁺Cl⁻ ionic complex in 20–50% yield depending on the type of phosphines used (eq. 2). Further addition of SnCl₂ (Pt/Sn = 1/1) immediately resulted in the quantitative formation of [PtClP(P–P)]⁺[SnCl₃]⁻. (The abbreviations used for bisphosphines in this work are

the followings: DPPE = 1,2-bis(diphenylphosphino)ethane, PROPHOS = (+)(R)-1,2-bis(diphenylphosphino)propane, VALPHOS = (+)-(R)-1,2-bis(diphenylphos-phino)-3-methyl-butane, CHIRAPHOS = (−)-(2S,3S)-2,3-bis(diphenylphosphino)-butane, BDPP = (−)-(2S,4S)-2,4-bis(diphenylphosphino)pentane, BPPM = (−)-(2S,4S)-4-(diphenylphosphino)-2-[(diphenylphosphino)methyl]pyrrolidine.)

$$PtCl_2(P-P) \xrightarrow{P} [PtClP(P-P)]^+[Cl]^- \xrightarrow{SnCl_2} [PtClP(P-P)]^+[SnCl_3]^- \qquad (2)$$
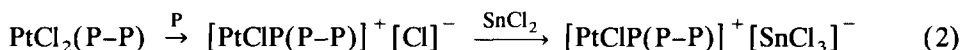
P–P =	DPPE	P =	PPh₃
	PROPHOS		PPh₂(2-Py)
	VALPHOS		PBu₃
	CHIRAPHOS		
	BDPP		
	BPPM		

The $^{31}P\{^1H\}$ NMR spectra (see Table 1) clearly show the presence of three different phosphorus atoms. One of them is *trans* to the Cl in the square-planar cation (the J(Pt–P) coupling constants are aproximately 3500 Hz) and two of the 3 phosphorus atoms are *trans* to each other (the J(Pt–P) coupling constants are < 2400 Hz). In most cases at 32.19 MHz the latter phosphorus atoms form a typical AB coupling system, with weak outside lines of the pattern due to the relatively large J(P–P,*trans*) coupling constants (400 Hz). The J(P–P,*cis*) coupling constants are in the range 15–25 Hz (Table 1). However, the 121.42 MHz $^{31}P\{^1H\}$ NMR spectrum can be interpreted as a first-order spectrum (Fig. 1).

The ^{31}P chemical shifts are strongly dependent on the chelate ring-size. They are larger in the 5-membered than in the 6- or 7-membered rings. The substituents on the carbon adjacent to the phosphorus atoms of the chelating bisphosphines increase the chemical shifts.

When ditertiary phosphines without C-2 symmetry (VALPHOS, PROPHOS) are used the addition of the monophosphines results in the formation of both of the possible species. The ratio of the two isomers is approximately 1/1 and 1/2 in the case of PROPHOS and VALPHOS, respectively. In the BPPM-containing complex the monodentate phosphine selectively coordinates *trans* to the phosphorus attached to the *exo*-methylene carbon. The presence of two species of very similar structure is probably due to restricted rotation about the N–C(O) band (the ratio of the two amide conformations of the 'Boc group, *syn* and *anti*, is 1/1 at 30 °C.) [5], but the presence of two chelate conformations cannot be excluded [2,6].

The ionic character of the species obtained was proved by the following observations: i) there are no tin satellites in the ^{31}P NMR spectra, which is consistent with the presence of $SnCl_3^-$ as a counterion (the tin is not directly bonded to the platinum); ii) the spectra of the complexes formed immediately after addition of monophosphine are the same as that of the final product; iii) exactly the same spectra were obtained when NaBPh₄ was used instead of $SnCl_2$, giving [PtClP(P–P)]⁺[BPh₄]⁻ and NaCl (P–P = DPPE, BDPP; P = PPh₃), showing that change in the counterion does not affect the ^{31}P NMR signals from the complex cation; iv) the equivalent conductivity of the ionic [PtCl(PPh₃)(P–P)]⁺[SnCl₃]⁻ is

Table 1

^{31}P NMR spectroscopic data for [PtCl(P)(P–P)]$^+$ cationic complexes

P	P–P	P^A		P^B		P^C		J(P–P) coupling constants (Hz)		
		δ (ppm)	J(Pt–P) (Hz)	δ (ppm)	J(Pt–P) (Hz)	δ (ppm)	J(Pt–P) (Hz)	J$_{AB}$	J$_{BC}$	J$_{AC}$
PPh$_3$	DPPE	53.8	2404	46.0	3520	23.7	2380	7.0	16.0	389
PPh$_3$	PROPHOS	59.5	2400	35.4	3463	23.8	2380	10.4	16.1	385
		39.1	2378	48.2	3516	24.0	2402	13.5	14.5	387
PPh$_3$	VALPHOS	55.9	2363	30.3	3477	23.2	2398	13.8	15.8	384
		34.8	2389	44.9	3511	23.1	2407	14.4	14.8	388
PPh$_3$	CHIRAPHOS	51.1	2345	42.7	3454	24.3	2406	17.8	14.8	381
PBu$_3$	CHIRAPHOS	49.1	2174	40.4	3500	9.6	2315	17.5	15.0	362
PPh$_3$	BDPP	22.1	2368	12.1	3454	14.6	2309	20.0	25.4	392
PPh$_2$Py	BDPP	19.8	2410	13.9	3494	15.7	2366	21.2	23.2	393
PBu$_3$	BDPP	18.0	2135	13.2	3522	10.1	2272	28.0	15.9	370
PPh$_3$	BPPM	24.5	2406	30.3	3588	18.0	2292	16.7	20.5	400
		24.6	2424	30.3	3588	17.9	2314	16.8	20.7	399

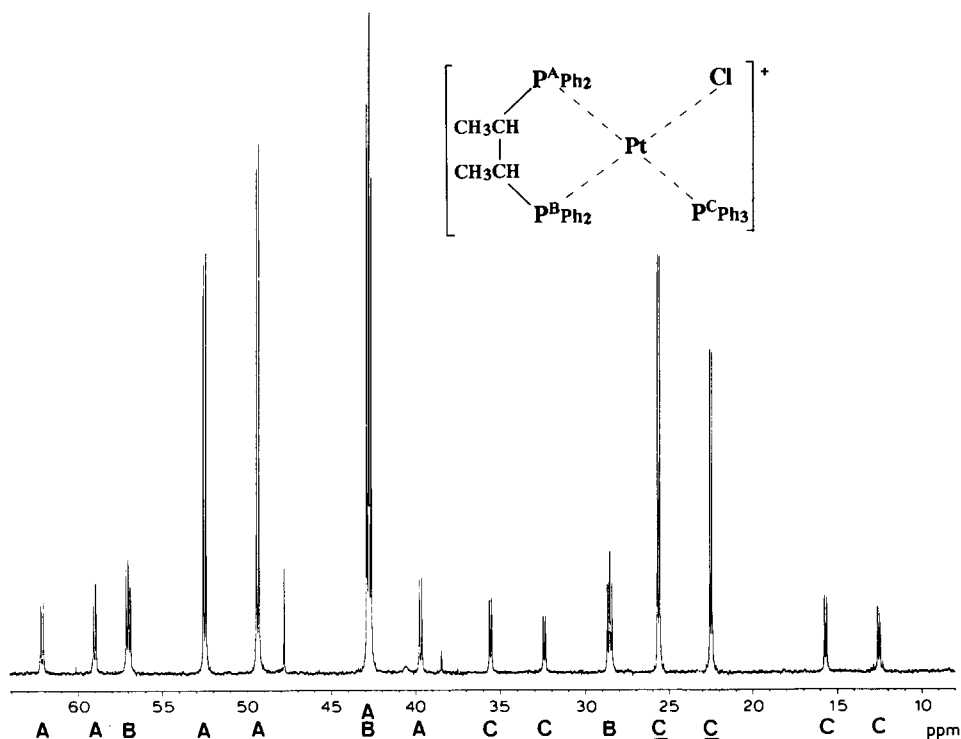Fig. 1. The $^{31}P\{^{1}H\}$ NMR spectrum of $[PtCl(CHIRAPHOS)(PPh_3)]^+$ at 121.42 MHz. (The underlined capital letters indicate the phosphorus atoms bonded to platinum isotopes other than ^{195}Pt ($I = 1/2$).)

larger than that of $PtCl(SnCl_3)(P-P)$ by almost two orders of magnitude, and even the addition of PPh_3 to $PtCl_2(P-P)$ results in formation of ionic complexes. (Λ_0 for $PtCl(SnCl_3)(DPPE)$: 0.74 cm^2 ohm^{-1} mol^{-1}, for $PtCl_2(DPPE) + PPh_3$: 12.6 cm^2 ohm^{-1} mol^{-1}, for $[PtCl(PPh_3)(DPPE)]^+[SnCl_3]^-$: 39.6 cm^2 ohm^{-1} mol^{-1}.)

High-pressure NMR investigations are planned to determine whether the trichlorostannato-ligand is coordinated directly to the platinum in the catalytically active species at these molar ratios under "oxo-conditions" as suggested previously [7]. The simultaneous coordination of both the bidentate and monodentate phosphine to the platinum has been confirmed in this work. An additional problem to be solved is whether the bidentate phosphines can possibly function in the monodentate mode in catalytically active intermediates containing both phosphine ligands. Such species could impose different steric requirements on the coordination of the substrate, resulting in different optical yields in enantioselective hydroformylation.

Experimental

The $PtCl_2P_2$-type complexes were prepared from $PtCl_2(PhCN)_2$ by a standard method [8]. The anhydrous $SnCl_2$ used for the preparation of ionic complexes was made by dehydrating $SnCl_2 \cdot 2H_2O$ with a stoichiometric amount of acetic anhydride followed by washing with ether.

Some of the ionic complexes investigated in solution by NMR spectroscopy (e.g. [PtCl(CHIRAPHOS)PPh$_3$]$^+$SnCl$_3^-$ and [PtCl(BDPP)Ph$_2$PPy]$^+$SnCl$_3^-$) were isolated as white powders by adding cold pentane dropwise to their CH$_2$Cl$_2$ solutions. The microanalytical data for the isolated complexes were satisfactors. The ^{31}P NMR spectra recorded before and after isolation were identical.

The ^{31}P NMR spectra were recorded for CD$_2$Cl$_2$ solutions on a Varian CFT-20 or Varian Unity 300 spectrometer operating at 32.19 and 121.42 MHz, respectively. The signals were referenced to the external 85% H$_3$PO$_4$. (A positive sign indicates a shift to lower field.) The samples used for NMR investigations were prepared under argon.

The conductivity measurements were carried out under argon in freshly distilled CH$_2$Cl$_2$.

Aknowledgements

References

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