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The Reaction of $[PtCl_4]^{2-}$ with 1,1,4,7,10,10-Hexaphenyl-1,4,7,10-Tetraphosphadecane: Complete Product Selectivity via Non-coordinating Anions and Isolation of Two Intermediates

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Abstract

The reaction of $[PtCl_4]^{2-}$ with 1,1,4,7,10,10-hexaphenyl-1,4,7,10-tetraphosphadecane (P_4) leads to four different products due to the formation of intermediates and the presence of two different diastereomers of P_4. The four complexes can be separated using non-coordinating anions. $[PtCl(P_4)](BF_4)$ (**1**), $[PtCl(P_4)](BPh_4)$ (**2**), chiral $[Pt(P_4)](BPh_4)_2$ (**3**) and *meso*-$[Pt(P_4)](BPh_4)_2$ (**4**) have been characterized by elemental analyses, ^{195}Pt and ^{31}P NMR spectroscopy, and in one case (**3**) by a preliminary X-ray diffraction analysis. In the five-coordinate complex **1** P_4 has a tetrahedral arrangement. **2** is also five-coordinate, the chloride occupying the apical and P_4 the four basal positions of a square pyramid. **3** and **4** have four-coordinate square-planar structures where the X-ray structure of **3** shows it to be the chiral form of the two possible diastereomers. **4** is therefore supposed to be the *meso* form. A steric effect as a possible reason for the observed diastereoselective action of $Na(BPh_4)$ is discussed.

Introduction

In the absence of non-coordinating anions replacement of the chlorides in $[PtCl_4]^{2-}$ by 1,1,4,7,10,10-hexaphenyl-1,4,7,10-tetraphosphadecane (P_4), first investigated by King and co-workers [1], leads to a mixture of three complexes. This is a common difficulty in polyphosphine chemistry, where different stereoisomers are often formed [2, 3]. However, it is widely recognized, that non-coordinating anions and cations may alter the reactivity of corresponding counterions by ion pairing effects [4]. In the above reaction the reaction pathway is strongly influenced by the presence of non-coordinating anions. $NaBF_4$ leads to a complete product selectivity and the formation of only one product. Two further products are obtainable by initial addition of $Na(BPh_4)$. The first two products are shown to be intermediates. From one intermediate a fourth product is formed.

Results

It has been known for some time that P_4 has two different diastereoisomers due to the chiral nature of the internal phosphorus atoms: the chiral *R,R* and *S,S* diastereomer and the *meso*-(*R,S* and *S,R*) form [5]. At 300 MHz the two stereoisomers have similar but distinct ^{31}P NMR resonances and it has been shown that commercial samples of P_4 contain the high-melting *meso* isomer and the low-melting chiral isomer in the ratio 2/1 [6]. In this work commercial P_4 of the same composition has been used without separation of the two diastereomers.

Table 1 contains the various product distributions for the reaction of $[PtCl_4]^{2-}$ with P_4 in the absence and presence of non-coordinating anions. $NaBF_4$ leads only to one product $[PtCl(P_4)](BF_4)$ (**1**). $Na(BPh_4)$ leads to a mixture of an isomer of **1** with a different arrangement of P_4, $[PtCl(P_4)](BPh_4)$ (**2**), and $[Pt(P_4)](BPh_4)_2$ (**3**). **2** and **3** are easily separable, since only **2** is soluble in CH_2Cl_2. Addition of an equimolar amount of $Na(BPh_4)$ to CH_2Cl_2 solutions of **2** produces the other diastereomeric form of **3**, **4**.

In Fig. 1 the ^{195}Pt NMR spectra of **1** and **2** are shown. In Table 2 the ^{195}Pt and ^{31}P NMR data for all four complexes are summarized. The ^{195}Pt NMR spectrum of **1** (Fig. 1a) consists of a broad quintet, indicating that all four ^{31}P nuclei of P_4 occupy nearly identical magnetic sites, which is only possible in the case of a tetrahedral arrangement of P_4 in the five-coordinate complex **1**. At 253 K the signals sharpened indicating an exchange process at room temperature. The ^{31}P NMR spectrum of **1** is consistent with an AB_2C spin system also typical for a tetrahedral arrangement of P_4 in **1**, since corresponding tetrahedral platinum(0) complexes show the same AB_2C spectra: $[Pt(etp)(PPh_3)]$, where etp is bis(2-(diphenylphosphino)ethyl)phenylphosphine, and $[Pt(P_4)]$ have been prepared according to ref. 7; both complexes show AB_2C ^{31}P NMR spectra (at 40.4, 30.65, 26.9; and 44.2, 37.9, 29.3 ppm). No attempt was made to assign the two kinds of ^{31}P nuclei of P_4 in **1**, though it seems likely that A and

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TABLE 1. Product Distributions for the Reaction of $[PtCl_4]^{2-}$ with P_4 under Various Conditions

Non-coordinating anion (X^-)	T (K)	$[PtCl(P_4)]X$ th[b]	$[PtCl(P_4)]X$ sp[b]	$[Pt(P_4)]X_2$ chiral	$[Pt(P_4)]X_2$[a] *meso*
None ($X^- = Cl^-$)[c]	293	35		22	43
$(PF_6)^-$[c]	273	64		14	22
$(AsF_6)^-$[c]	273	90	3		7
$(BF_4)^-$	273	100			
$(BPh_4)^-$[d]	293		68	32	

[a] In %(*w*/*w*). [b] th = tetrahedral arrangement of P_4, sp = square-pyramidal. [c] From ^{31}P NMR spectral integrations. [d] By relative weights.

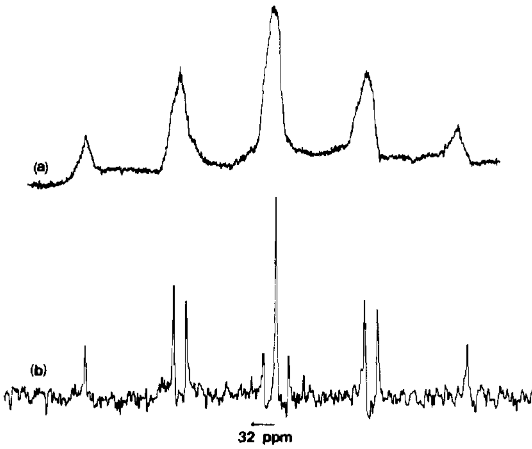

Fig. 1. 17.2 MHz $^{195}Pt\{^1H\}$ NMR spectra of (a) a CH_3NO_2 solution of 1 and (b) a CH_2Cl_2 solution of 2 at 300 K.

C correspond to the terminal $-PPh_2$ groups. At 233 K the ^{31}P NMR spectrum of **1** consists of a single broad line showing two shoulders, nicely corresponding to the above described ^{195}Pt NMR spectrum of **1**.

The ^{195}Pt NMR spectra of **2** (Fig. 1b), **3** and **4** consist of triplets of triplets produced by coupling of two equivalent $-PPh$ and two equivalent $-PPh_2$ groups in all cases. The ^{195}Pt resonances of all four complexes are shifted to higher fields compared with the corresponding value for a similar platinum(II) complex of a tripodal tetraphosphine, $[PtCl(PP_3)]Cl$, where PP_3 is tris(2-(diphenylphosphino)ethyl)phosphine and $\delta(^{195}Pt) = -4372$ ppm [8]. The $^1J(Pt-P)$ parameters are in the range expected for square-planar platinum(II) complexes containing only phosphorus ligands, the $^1J(Pt-PPh_2)$ coupling constants being typically larger than the $^1J(Pt-PPh)$ values [9]. The ^{31}P NMR spectra of **2**, **3** and **4** are consistent with A_2M_2 spin systems. Since phosphorus atoms as part of a five-membered ring are deshielded and the downfield shift increases nearly additively with the number of chelating five-membered rings to which a phosphorus atom is attached [10], one pair of phosphines is part of one five-membered chelate ring (with the ^{31}P chemical shift very similar to that found in $[Pt(Ph_2PCH_2CH_2PPh_2)_2]Cl_2$, $\delta(P) = 47.8$ ppm; ref. 8) and the second pair is attached to two chelating five-rings. From that it is clear, that the high-field signal is attributed to the $-PPh_2$ groups and the low-field one to the $-PPh$ groups in Table 2. The $^2J(PPh, PPh_2)$ values are typical for $^2J(P, P_{trans})$ couplings for two phosphines [9, 11].

Both the ^{195}Pt and ^{31}P NMR data are consistent with square-planar arrangements of P_4 in **2**, **3** and **4**. In **2** elemental analysis, colour and reactivity towards nucleophiles [12] indicate the presence of chloride as a fifth ligand. Therefore a square-pyramidal structure is suggested for **2**, with the chloride occupying the apical position. The structure of **3** has been revealed by an X-ray structure analysis [13]. The *trans* positions of the phenyl groups at the two

TABLE 2. Platinum-195 and Phosphorus-31 NMR Data for **1**, **2**, **3** and **4**[a]

Compound	δ(Pt)	$^1J(Pt-P)$		δ(P)		
1	−5084(q)	2233		46.1, 43.4, 38.0		
		$^1J(Pt-PPh)$	$^1J(Pt-PPh_2)$	δ(PPh)	$\delta(PPh_2)$	$^2J(PPh, PPh_2)$
2	−5098(tt)	2279	2588	86.7	42.3	290
3	−5110(tt)	2137	2403	92.3	39.2	275
4	−5103(tt)	2100	2432	89.1	44.7	280

[a] δ [ppm], J [Hz], 300 K; **1**, **3** and **4** were measured in CH_3NO_2, **2** was run in CH_2Cl_2; an internal deuterium lock was used; q = quintet, tt = triplet of triplets.

central phosphorus atoms of P_4 in **3** indicate that **3** is the chiral form of the two possible diastereomers. Since **4** can be easily produced from **2** and shows the same elemental composition as **3**, **4** is assigned to the *meso*-diastereomer of $[Pt(P_4)](BPh_4)_2$. This is also in agreement with the observed product distributions of **2** and **3** in an approximate ratio 2/1 reflecting the diastereomer distributions in commercial P_4.

Discussion

In **1** no indication for a second diastereomer was observed. This might be due to the low yield for **1** and the synthetical preference of one diastereomer. Since four-coordinate platinum(II) complexes are invariably square planar [14], loss of the chloride as fifth ligand is only possible after rearrangement of P_4 from tetrahedral in **1** to square planar in **2**. By the diastereoselective action of $Na(BPh_4)$ the chloride remains coordinated only in the case of **2** containing *meso*-P_4. This illustrates the fact that for P_4 complexes small changes in ligand geometry can have profound effects on their coordination chemistry [6] and might be a consequence of the steric differences in phenyl substitution at the central phosphorus atoms of P_4 between **2** (*cis* positions) and its chiral counterpart (*trans* positions) which seem to allow the formation of a contact ion pair with $(BPh_4)^-$ only in the case of **2**. Both **1** and **2** have very unusual platinum(II) coordination geometries. **1** is possibly best described as a tetrahedral arrangement of P_4 with the chloride capping a tetrahedral face, a configuration type found for hydrides of composition HML_4 [15]. However, more work has to be done to reveal the very nature of complexes of type **1** and **2**.

Experimental

Reagent grade chemicals were used as received unless stated otherwise. 1,1,4,7,10,10-Hexaphenyl-1,4,7,10-tetraphosphadecane (P_4) was purchased from Strem Chemical Co. $NaPF_6$ was purchased from Aldrich Chemical Co., $LiAsF_6$ from Ventron, $NaBF_4$ from Fluka, and $Na(BPh_4)$ was of purissimum grade quality and received from Merck-Schuchardt. All solvents were obtained from Fluka. Solvents used for NMR measurements and for crystallization purposes were of purissimum grade quality. $Na_2PtCl_4 \cdot 4H_2O$ was prepared from platinum metal.

Fourier-mode, broad-band proton-decoupled ^{195}Pt and ^{31}P NMR spectra were obtained by use of a Bruker WP-80 spectrometer. Positive chemical shifts are downfield from 1.0 M Na_2PtCl_6 and 85% H_3PO_4 used as external standards. Elemental analyses were obtained with a Heraeus EA 425 elemental analyzer.

A Schlenk apparatus and oxygen-free, dry Ar were used in the syntheses of all complexes. Solvents were degassed by several freeze–pump–thaw cycles prior to use.

Complex 1

To $Na_2PtCl_4 \cdot 4H_2O$ (0.3 mmol, 0.115 g) and $NaBF_4$ (0.6 mmol, 0.006 g) in water a solution of P_4 (0.3 mmol, 0.201 g) in CH_2Cl_2 was added. Then EtOH was added under stirring until a yellow precipitate formed. The reaction was carried out at 273 K. **1** was filtered off, washed with water, and dried *in vacuo*: yield 0.148 g (50%), melting point (m.p.) = 194–195 °C. *Anal.* Calc. for $C_{42}H_{42}BClF_4P_4Pt$: C, 51.1; H, 4.3. Found: C, 50.7; H, 3.9%.

Complexes 2 and 3

To $Na_2PtCl_4 \cdot 4H_2O$ (0.6 mmol, 0.230 g) and $Na(BPh_4)$ (0.9 mmol, 0.308 g) in water a solution of P_4 (0.6 mmol, 0.402 g) in CH_2Cl_2 was added. Then EtOH was added under stirring until a yellow precipitate formed. The reaction was carried out at 293 K. **2** and **3** were filtered off, washed with water, and dried *in vacuo*. The yellow powder was partly dissolved in CH_2Cl_2 and filtered. Evaporation of the yellow filtrate lead to a yellow powder which was dried *in vacuo*. **2**: yield 0.447 g (61%); m.p. = 135–137 °C. *Anal.* Calc. for $C_{66}H_{62}BClP_4Pt$: C, 64.9; H, 5.1. Found: C, 64.5; H, 5.5%. The insoluble part was washed with CH_2Cl_2, recrystallized from CH_3NO_2, and dried *in vacuo*. **3**: colourless crystals, yield 0.210 g (29%); m.p. = 225–228 °C dec. *Anal.* Calc. for $C_{90}H_{82}B_2P_4Pt$: C, 71.8; H, 5.5. Found: C, 71.8; H, 5.9%.

Complex 4

2 (0.1 mmol, 0.122 g) was dissolved in CH_2Cl_2 and $Na(BPh_4)$ (0.1 mmol, 0.034 g) was added. The solution was stored at 243 K for one week and a white precipitate gradually formed. **4** was filtered off, washed with CH_2Cl_2 and water, and dried *in vacuo*: yield 0.045 g (30%); m.p. = 236–239 °C dec. *Anal.* Calc. for $C_{90}H_{82}B_2P_4Pt$: C, 71.8; H, 5.5. Found: C, 71.5; H, 5.7%.

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