Three Identical Bidentate Ligands complexed with Penta- and Hexa-co-ordinate Phosphorus: Stereospecificity of the $P^V \longrightarrow P^{VI}$ Transformation

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The substitution of bidentate ligands for chlorine, in benzene solution, for phosphorus pentachloride, leads to the equilibrated phosphoranes (4) ⇌ (5). Because of its insolubility the bridged bispentaoxyphosphorane (4a) has been isolated. The addition of a weak base (dimethylformamide) in this system shows the existence of the (5) ⇌ (6) equilibrium. A stereospecific transformation $P^V \longrightarrow P^{VI}$ is obtained by the addition of an optically active strong base, (−)-brucine.

WITHIN the framework of our studies of hexaco-ordinated phosphorus anions of the trischelate type, we have synthesized first a molecule bearing three different bidentate ligands [1] and secondly one with two identical ligands.[2] In this paper we present the synthesis of two hexaco-ordinated species bearing three identical ligands, pyrocatechol and 2,2'-dihydroxybiphenyl. We have resumed the study of the reaction between pyrocatechol and phosphorus pentachloride previously described.[3-5] Our work shows: (i) the existence of an equilibrium between pentaco-ordinated intermediates; (ii) the leading part played by a base in the passage from penta- to hexa-co-ordination; and (iii) the stereospecificity of this transformation.

RESULTS AND DISCUSSION

The progressive substitution of phosphorus pentachloride by pyrocatechol in benzene was followed by [31]P n.m.r. spectroscopy and titration of the evolved hydrogen chlorine (Table 1). Compounds (2a) and (3a) (δ −27 and −9, respectively)† already described,[3-8] appeared first (Scheme 1).

TABLE 1

Products formed by progressive substitution of phosphorus pentachloride by pyrocatechol

| Compound | $\delta_p{}^b$ | Product (%) obtained by adding n equivalents of pyrocatechol ^{a} | | | | | | | | Base |
		0	0.5	1	1.5 ^{d}	2n ^{d}	2.5	3	>3	added ^{c}
(1)	−82	100	65	30	15	0	e			
(2a)	−27		20	37	25	0	e			
(3a)	−9		15	33	40	70	e			
(4a)	−31				20	30	e	20	10	
(5a)	−29						e	80	90	
(6a)	−84						e			100

^{a} In benzene. ^{b} Chemical shifts are positive to low field related to 85% H_3PO_4. ^{c} Triethylamine or brucine or excess of DMF. ^{d} Precipitation starts at this point. ^{e} Insoluble products.

During the addition of a third half-equivalent (n 1.5, Table 1) of pyrocatechol, a white precipitate forms. The quantity of this precipitate increases up to n 2.5. At this point, the n.m.r. spectrum can no longer be recorded. Further addition of pyrocatechol gradually dissolves the precipitate. When isolated it is weakly soluble in non-polar solvents but in methylene chloride the ^{31}P spectra

† For the sign of the chemical shift, see Experimental section.

give a singlet at δ −31. This chemical shift is the same as that observed in benzene solution when n is different from 2.5 (the increase of the solubility of the precipitate
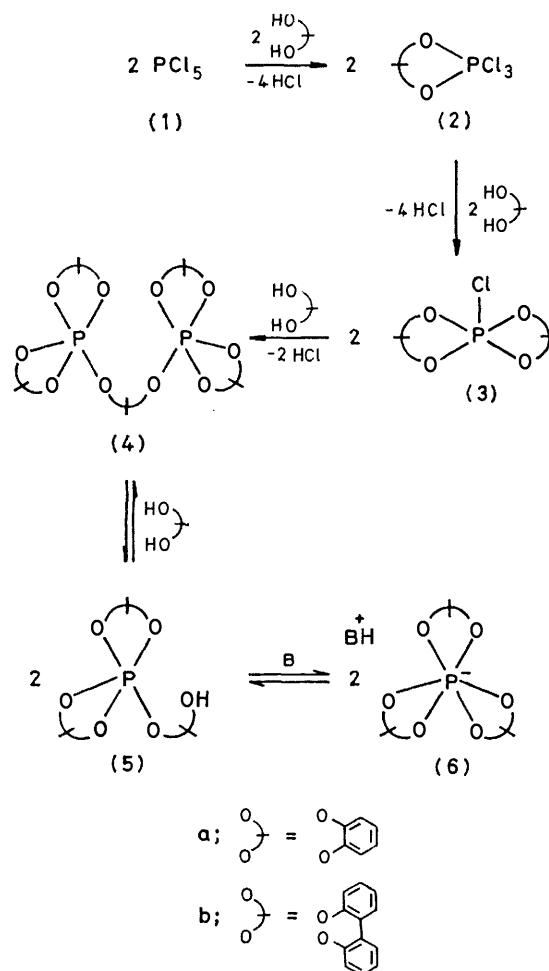
SCHEME 1 Progress of chlorine substitution of phosphorus pentachloride by bidentate ligands derived from pyrocatechol and 2,2'-dihydroxybiphenyl. B = base [DMF, NEt₃, or (−)-brucine]
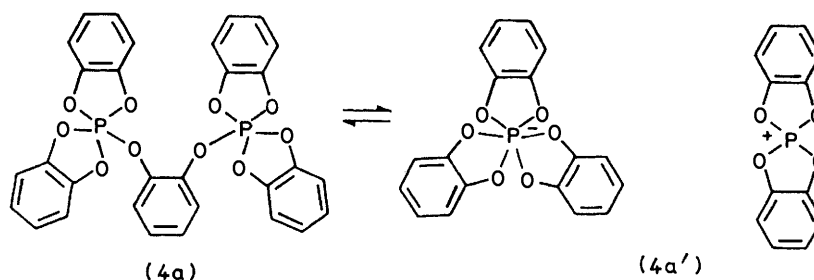
in this last case is probably due to the presence of other compounds). Elemental analysis of the isolated precipitate suggests the formula $C_{30}H_{20}O_{10}P_2$ and we assign the singlet at δ −31 to formula (4a). This bis-pentaoxyphosphorane structure had already been estab-

lished by Anschutz *et al.*[3,*] Since then other 'bridged pentaco-ordinate spirane' structures have been observed for phosphorus [9] and arsenic derivatives.[10]

The addition of a stoicheiometric quantity of DMF as base to a methylene chloride solution of (4a), at room temperature, does not change the ^{31}P n.m.r. spectrum. In the same solvent, (4a) reacts with $Cl^-NEt_4^+$ to give the hexaco-ordinated anion (6a),[11,12] the phosphoranes (2a) and (3a), and a P^{IV} species (δ +12.5). We can interpret this, either as attack of a chloride anion on a pentaoxyphosphorane followed by rearrangement, or as the reaction of pre-existing negatively charged P^{VI} and positively charged P^{IV} ions. Thus (4a) can exist in the solution in equilibrium with the ion pair (4a') (Scheme 2). This assumption is in agreement with the reactivity and insolubility of (4a) in non-polar solvents.

The variation of the apparent molecular weight of (4a) with concentration (Figure 1), determined by ebullio-metry in benzene, is also consistent with the existence of ionic forms in solution.[13,14] We were not able to determine the chemical shift of the possible ionic structures, as Hellwinkel did for bisphenylenephosphonium derivatives,[15] and as Schmidpeter did [16] by stabilizing a hexaco-ordinated cation with pyridine, but it is possible that the observed chemical shift of (4a) is average (Scheme 2).

Finally synthesis of (4a) has been carried out in good yield by adding a half-equivalent of pyrocatechol, in benzene or CH_2Cl_2 to (3a). Compound (5a) which gives a

we changed the sequence of introduction of the reagents, *i.e.* we introduced compound (3a) to an excess of pyro-catechol. This leads to the same equilibrium between
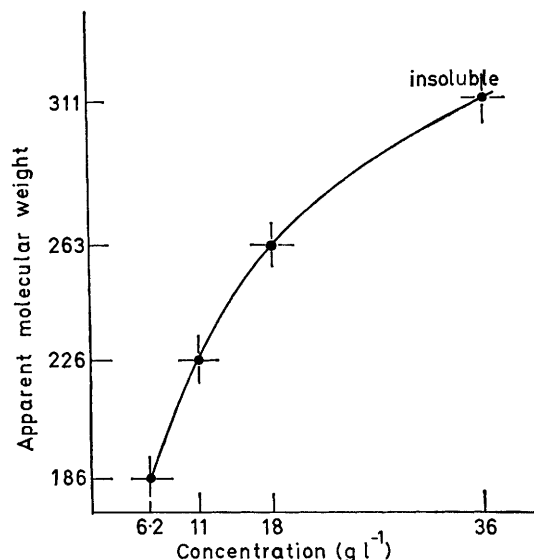

FIGURE 1   Determination of the apparent molecular weight of (4a), in benzene solution, by ebulliometry

(4a) and (5a). In this case (4a) can no longer be formed by the reaction of (3a) with (5a).

The substitution of phosphorus pentachloride by 2,2'-dihydroxybiphenyl was carried out under the same con-

(4a) ⇌ **(4a')**

SCHEME 2

signal at δ —29 (C_6H_6) is the result of the last substitution step on a pentacovalent phosphorus atom. Its formation has already been considered as the necessary intermediate towards hexaco-ordination.[5,17,18] The appearance of (5a) together with (4a) can be observed in the n.m.r. spectra. The i.r. spectra of (5a) and the analytical data show the presence of free pyrocatechol.

One can conclude that in benzene solution, (5a) is in equilibrium with the soluble part of (4a) (Scheme 3). The observed substitution sequence (3a) → (4a) → (5a) seems logical if we take into account the high reactivity of (3a). In this case, the appearance of (4a) is the result of the reaction of (5a) with the remaining (3a) (Scheme 4). In fact (4a) and (5a) are in equilibrium. To show the existence of the equilibrium between (4a) and (5a),

ditions as for pyrocatechol (Table 2) so as to obtain a seven-membered ring attached to the phosphorus atom.[19-22]

Compared with the above example, the adducts are

(4a) ⇌ 2

(5a)
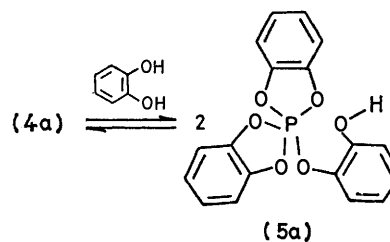
SCHEME 3

not soluble in refluxing benzene until two equivalents of 2,2'-dihydroxybiphenyl have been added. The removal of hydrogen chloride indicates the progress of substitution. We have not characterized the expected

intermediates (2b) and (3b) because of their insolubility. The addition of more than two equivalents of 2,2′-dihydroxybiphenyl starts to dissolve the insoluble adducts.

When 2.5 equivalents have been added, the ^{31}P n.m.r. spectrum of the mixture shows a singlet at δ —48.8.

TABLE 2

Products formed by progressive substitution of phosphorus pentachloride by 2,2′-dihydroxybiphenyl

Compound	$δ_p$ [b]	Products (%) obtained by adding n equivalents of 2,2′-dihydroxybiphenyl [a]					
		0 ⟶ 2	2.5	3	>3	DMF added [d]	NEt₃ or brucine added
(1)	—82	100	0				
c		c					
c		c					
(4b)	—48.8	c	100	20	10	10	
(5b)	—49.6	c		80	90	90	
(6b)	—93	c					100

[a] In benzene. [b] Chemical shifts are positive to low field related to 85% H₃PO₄. [c] Insoluble products, probably (2b) and (3b). [d] No change upon adding DMF, a weak base (see Table 1).

With further addition, at n 3, two signals at δ —49.6 and —48.8, in the ratio 80:20, appear. The compound with δ —48.8 and empirical formula $C_{60}H_{40}O_{10}P_2$ was isolated and assigned structure (4b). This is in equilibrium with the species giving a peak at δ —49.6 and by analogy, we assigned structure (5b) to this compound.

Addition of a base to the equilibrium (4) ⇌ (5), leads to hexaco-ordination at the phosphorus atom

(3a)
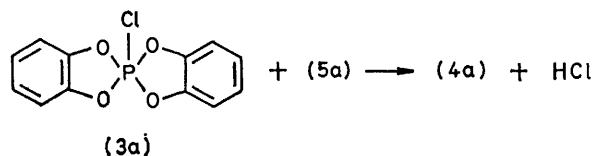
SCHEME 4

[compounds (6)]. In the case of the pyrocatechol derivatives the addition of DMF, a weak base, is enough to establish an equilibrium between the penta- and hexaco-ordinated structures.[23] Starting from the equilibrium [(4a):(5a) = 20:80] in benzene (Figure 2a), the progressive addition of this base induces a gradual shift of the ^{31}P signal at δ —29 [corresponding to (5a)] up to δ —84 and a decrease of the signal at δ —31 [(4a)] until it collapses (Figure 2a—d). The changes in the n.m.r. spectra are related to the process (4a) ⇌ (5a) ⇌ (6a) in which the transformation between (5a) and (6a) is too fast to allow these species to be distinguished.

These observations result from (i) slow exchange between the phosphoranes (4a) and (5a), (ii) fast exchange between the P^V and P^{VI} compounds, and (iii) the variation in the ratio of these last two species.[24] These facts explain the apparent discrepancy of the chemical shifts attributed to (4a) and (5a) in the literature.[4,5]

The addition of strong bases such as triethylamine causes the precipitation of the hexaco-ordinate com-

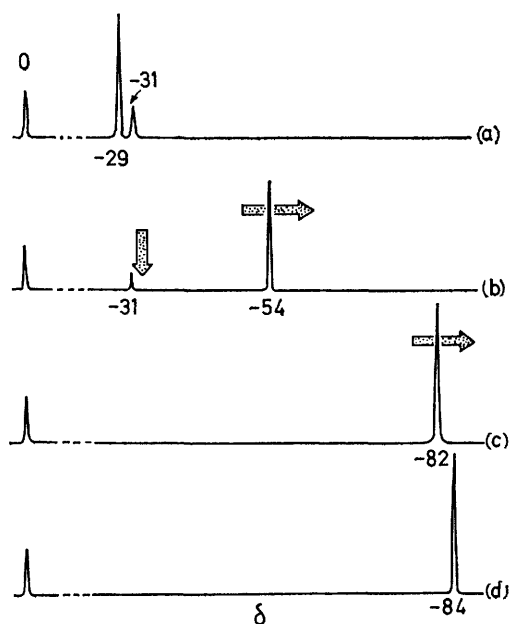pound. This molecule has been already described by Allcock et al.[11,12]

FIGURE 2 The equilibrium (4a) ⇌ (5a) ⇌ (6a) observed by ^{31}P n.m.r. spectroscopy after addition of a weak base (DMF) in benzene solution: (a) (4a) ⇌ (5a); (b) half equivalent of DMF added; (c) one equivalent of DMF added; (d) excess of DMF added. The arrows show the modifications of the signals

In order to prepare optically active adducts, we used one equivalent of (—)-brucine as base. The white precipitate which forms has the hexaco-ordinate structure (6a′). Moreover two peaks can be distinguished by ^{31}P n.m.r. spectroscopy (δ —84.4 and —84.5). The existence of these two signals is the consequence of a diastereoisomeric interaction between the brucinium cation and the two hexaco-ordinate anion helices Δ and Λ (Scheme 5). We have already studied such hexaco-ordinate species bearing a chiral ligand.[25,26] From the polarimetric and kinetic data for epimerization of the diastereoisomeric salt (6), it can be concluded that the P^{VI} anion released by the synthesis is not racemic (see Experimental section). Consequently, the transformation of the pentaco-ordinate compound into a hexaco-ordinate derivative is stereospecific.
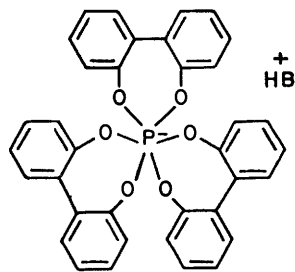
(C⁺ = brucinium)

(6a′)Λ   (6a′)Δ
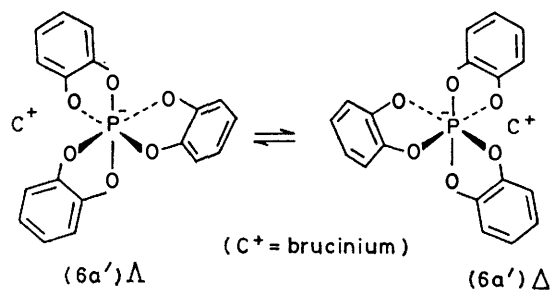
SCHEME 5

In the case of 2,2′-dihydroxybiphenyl the P^V ⟶ P^{VI} transformation does not occur upon addition of DMF: either this base is too weak for this purpose or the Lewis

acid character of the phosphorus atom in (5a and b) is different.

An insoluble hexaco-ordinate compound is obtained by addition of the stoicheiometric quantity of triethylamine

(6b or b')

(6b) B = NEt₃

(6b') B = brucine

in benzene solution. The ³¹P (δ —93.16) and ¹H n.m.r. parameters and the analytical data correspond to structure (6b).

Using brucine as a chiral base (see above) under the same conditions a hexaco-ordinated compound (6b') with δ —93.40 can be obtained. In this case the two diastereoisomeric salts were not easily distinguished by n.m.r. spectroscopy, but mutarotation was observed by polarimetry (see Experimental section).

EXPERIMENTAL

Reactions were carried out under nitrogen and followed by titration of the hydrogen chloride released. N.m.r. spectra were recorded on Perkin-Elmer R10 and R32 (with Fourier transformation) and Bruker HX 90 instruments. ³¹P Chemical shifts are negative at high field of 85% H₃PO₄. Optical rotations were taken on a Perkin-Elmer 141 polarimeter. I.r. data were recorded on Beckman 20 A spectrophotometer. Apparent molecular weights in benzene solution were determined with a Gallenkamp MW 140 ebulliometer.

Compounds from Table 1.—Phosphorus pentachloride (1.04 g, 0.005 mol) was dissolved in refluxing benzene (5 ml) and pyrocatechol was added in portions each of 0.275 g, 0.0025 mol. When the expected quantity of hydrogen chloride had evolved, a portion was taken for n.m.r. spectroscopy and then returned to the reaction mixture.

1,2-*Bis{2,2'-spirobi(1',2'-benzo[1,3,2]dioxaphospholan)-2-yloxy}benzene* (4a). Compound (3a) (2.82 g, 0.01 mol) was dissolved in refluxing benzene (25 ml) and crystallized pyrocatechol (0.55 g, 0.005 mol) was introduced into the solution. The reaction was carried out under nitrogen and 90% of the expected hydrogen chloride was released. Washing and drying gave a precipitate of (4a) (85%) (Found: C, 59.9; H, 3.45; P, 10.2. C₃₀H₂₀O₁₀P₂ requires C, 59.8; H, 3.3; P, 10.3%); δ_P (CH₂Cl₂) —31. To a solution of ClNEt₄ (0.55 g, 0.0033 mol) in CH₂Cl₂ (10 ml), (4a) (2.01 g, 0.0033 mol) dissolved in CH₂Cl₂ (50 ml) was added. After 20 h, the mixture was concentrated, δ_P (CH₂Cl₂) —82 (33%), —27 (17%), —9 (17%), and +12.5 (33%).

Equilibrium (4a) ⇌ (5a). PCl₅ (2.08 g, 0.01 mol) was dissolved in refluxing benzene (30 ml). Crystallized pyro-

catechol (3.3 g, 0.03 mol) was added under nitrogen. 80% of the theoretical amount of hydrogen chloride was released after 10 h. The product obtained gives two ³¹P n.m.r. signals, δ_P —29 (80%) (5a) and —31 (20%) (4a). The reaction of (3a) with one equivalent of pyrocatechol leads to the same results. The i.r. spectra showed, near a broad band at 3 370 cm⁻¹, two narrow ones at 3 570 and 3 610 cm⁻¹ typical of free pyrocatechol. This was also confirmed by elemental analysis.

Compound (6a'). The addition of (—)-brucine (3.94 g, 0.01 mol) dissolved in benzene to the (4a) ⇌ (5a) equilibrium mixture gave a precipitate instantly. Washing and drying yielded *brucinium* 2,2',2''-*spirotri*[1,3,2-*dioxaphospholan*]*ate* (85%), δ_P (CDCl₃) —84.40 and —84.54 (Found: C, 65.9; H, 5.7; N, 3.45; P, 3.5. C₄₁H₃₉N₂O₁₀P requires C, 65.6; H, 5.2; N, 3.75; P, 4.15%). Compound (6a') (22.48 × 10⁻³M) in DMF solution shows variation of rotation with time, the consequence of epimerization of the diastereoisomeric salt. The experimental first-order rate constant k is 104 × 10⁻⁵ s⁻¹ at —20 °C. The experimental infinite rotation $[\alpha_\infty]_{436}^{-20.3}$ is —37° with $[\Phi_\infty]_{436}^{-20.3}$ —280°. Extrapolation to time 0 gives $[\alpha_0]_{436}^{-20.3}$ 196° with $[\Phi_0]_{436}^{-20.3}$ 1 474°. The rotations of brucinium chloride under the same conditions are $[\alpha]_{436}^{-20.3}$ —28°, $[\Phi]_{436}^{-20.3}$ —121° ($c = 18.85 ×$ 10⁻³). These results show that the anion is not completely racemized at equilibrium (Pfeiffer effect [27]) and one helical anion is largely predominant in the starting material.

Compounds from Table 2.—Phosphorus pentachloride (2.08 g, 0.01 mol) was dissolved in refluxing benzene (25 ml). 2,2'-Dihydroxybiphenyl was added in portions each of 0.93 g, 0.005 mol. The progress of the reaction was followed as before.

Compound (4b). PCl₅ (2.08 g, 0.01 mol) was dissolved in refluxing benzene (60 ml) and crystallized 2,2'-dihydroxybiphenyl (4.65 g, 0.025 mol) was added. The intermediate precipitate disappeared when 90% of the expected hydrogen chloride had evolved. Addition of hexane precipitated 2,2'-*bis{2,2'-spirobi(dibenzo*[d,f][1,3,2]*dioxaphosphepin]-2-yloxy}biphenyl* (Found: C, 73.3; H, 4.8; P, 5.7. C₆₀H₄₀O₁₀P₂ requires C, 73.3; H, 4.05; P, 6.3%), δ_P (C₆H₆) —48.8.

Compound (6b). 2,2'-Dihydroxybiphenyl (5.58 g, 0.03 mol) were dissolved in refluxing benzene (100 ml). PCl₅ (2.08 g, 0.01 mol) without solvent was added. 80% of the expected hydrogen chloride was evolved. At this point, the ³¹P n.m.r. spectrum of the solution shows two signals, δ —48.8 (4b) and δ —49.6 (5b), resulting from the equilibrium between these two species. Triethylamine (1.01 g, 0.01 mol) was added and *triethylammonium* 2,2',2''-*spirotri-(dibenzo*[d,f][1,3,2]*dioxaphosphepin)ate* (6b) precipitated (75%) (Found: C, 74.3; H, 6.05; N, 1.95; P, 4.35. C₄₂H₄₀NO₆P requires C, 73.55; H, 5.85; N, 2.05; P, 4.5%), δ_P ([²H₆]Me₂SO) —93.16.

Compound (6b'). Under the conditions above, one equivalent of (—)-brucine (3.92 g, 0.01 mol) was added instead of triethylamine. The *brucinium salt* (6b') precipitated (90%) (Found: C, 73.95; H, 5.45; N, 2.35; P, 2.5. C₅₉H₅₁N₂O₁₀P requires C, 72.4; H, 5.2; N, 2.85; P, 3.15%), δ_P ([²H₆]Me₂SO) —93.40. Although diastereoisomerism was not easily detected by ³¹P n.m.r. spectroscopy, the variation of the rotation of the solution of (6b') with time is the result, as for (6a'), of epimerization. In DMF solutions (c 20 × 10⁻³M) at —20 °C the experimental first-order rate constant k is 77.10⁻⁵ s⁻¹ and the corresponding barrier $\Delta G^\ddagger$ 18.3 kcal mol⁻¹.

According to the experimental conditions the ^{31}P n.m.r. spectra of compounds (4b), (5b), (6b), and (6b') gives an additional singlet at δ -5 with variable intensity. A drop of water added to the n.m.r. sample collapses the spectrum to this single signal at δ -5. Consequently it results from hydrolysis of the pentaco-ordinate phosphorus compound to give a phosphate.

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