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NMR EVIDENCE FOR NEW PHOSPHORUS HALIDES

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Abstract—Reaction of P_4 with Br_2 or I_2, followed by treatment of product solutions with halide substitution reagents, allowed the identification by NMR of low concentrations of *exo,exo*-$P_4Cl_nBr_{2-n}$(**1**), *exo,endo*-$P_4Cl_nBr_{2-n}$(**2**), *symm*-P_7X_3 ($X = Br$ or I)(**3**) and $P_2X_nY_{4-n}$ (X and Y = two of Cl, Br, I).

Reaction of white phosphorus, P_4, with I_2 leads to P_2I_4 or PI_3, depending on the stoichiometry taken, and with Br_2 to PBr_3. For over a century there has been speculation on the mechanisms of these reactions and on the possibility of other products,[1] — when ^{31}P NMR was used to monitor the system:[2] complete breakdown of the P_4 cage to give PI_3 was found as the first step, followed by reaction of PI_3 with P_4 to give P_2I_4. Subsequently, P_2Br_4 has been made as a product of reduction of PBr_3 by iodide.[3] We now report four series of new compounds which can be studied in solutions in CS_2 resulting from reaction of P_4 with Br_2, I_2, or ICl, or as a result of reaction of these solutions with halide exchange reagents: these are binary or ternary "butterfly" halides P_4XY **1** and **2**, binary cage halides P_7X_3 **3** and ternary diphosphorus tetrahalides $P_2X_nY_{4-n}$.

RESULTS AND DISCUSSION

Procedures and products

Reaction in CS_2 of Br_2 with P_4 in molar ratio 1 : 2, gave, besides PBr_3, not only some P_2Br_4, but also the new butterfly molecules *exo,exo*-P_4Br_2 **1a** and *exo,endo*-P_4Br_2 **2a** as 0.5 mol% and 2 mol%, respectively of the phosphorus halide content. These were identified by ^{31}P NMR (see below) in the reaction mixture and were not isolated because of thermal instability. Their concentration was halved by decomposition in about 1 h at ambient temperature.

We found that P_4 in CS_2 does not react with PBr_3 at 20 °C in 3 days. Thus, in contrast to the P_4/I_2 system,[2] P_2Br_4 was not formed in the P_4/Br_2 system via PBr_3, nor were the butterfly molecules P_4Br_2 made by bromination of P_4 by PBr_3. Instead, it is very likely that molecules **1a** and **2a** were formed in the first step of bromination of P_4 by Br_2, but that the detected yields were low because of further bromination of **1a** and **2a** by Br_2. This route for removal of the butterfly molecules was much faster than their decomposition in the absence of Br_2, reported above, but was inhibited by the presence of excess P_4 which could compete for the Br_2. Because most of the added Br_2 went to make PBr_3, for which the required $Br_2:P_4$ ratio is 1 : 0.17, there was a large excess of P_4 present, even at the end of the addition of the Br_2. The ratio of excess P_4 present was found to control the yields of the butterfly molecules relative to PBr_3. Thus these were reduced to about one-third of the above values if a $Br_2:P_4$ ratio of 1 : 1 instead of 1 : 2 was taken, but were increased by a factor of only 1.5 if a 1 : 10 ratio was used. The isomeric ratio **1a** : **2a** was practically constant at 1 : 4 for all conditions tried.

Use of a more dilute solution of Br_2, rather than a lower $Br_2:P_4$ ratio, had negligible effect on the yields of **1a** and **2a**, since dilution of the Br_2 would slow down its reaction with these compounds and with the excess P_4 by the same factor. High dilution of the Br_2 did favour, however, the formation of P_2Br_4 relative to PBr_3: use of 0.083 mol dm^{-3} of Br_2 in CS_2 instead of 0.27 mol dm^{-3} yielded P_2Br_4 as 6.2 mol% instead of 2.7 mol% of the phosphorus

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halide products. This was accompanied by a trace (0.16 mol%) of the new cage molecule *symm*-P_7Br_3 **3b** (cf. *symm*-P_7I_3 **3a**, below), suggesting that expansion of the P_4 cage to the P_7 cage may have been by means of the PBr carbenoid, extruded from P_2Br_4.

Treatment with Me_3SnCl of solutions resulting from the P_4/Br_2 reaction gave solutions containing *exo,exo*-P_4ClBr **1b**, *exo,exo*-P_4Cl_2 **1c**, and the three remaining *exo,endo*-butterfly molecules **2b–2d**, as well as all the possible new molecules $P_2Cl_nBr_{4-n}$. Use of Me_3SiI instead of Me_3SnCl caused destruction of the butterfly skeletons, but gave, besides PI_3 and P_2I_4, a little of the new cage molecule *symm*-P_7I_3 **3a**. This was better made by direct reaction of CS_2 solutions of I_2 and P_4 in molar ratio $\frac{3}{2}:\frac{7}{4}$ at $-30°C$, giving PI_3, P_2I_4 and **3a** in molar ratio 27 : 71 : 2.

In general, the P_7X_3 structure **3** was formed to a significant extent only for X = I, while the butterfly P_4X_2 structures **1** or **2** were found only for X = Cl or Br. Compounds with the P_7 skeleton may be considered as derivatives of the $[P_7]^{3-}$ ion,[4] and consequently are formed when the available ligands are capable of supporting sufficient positive charge. Iodine and to some extent bromine now appear to fall into that category. When a solution containing PI_3, P_2I_4 and **3a** was treated with $HgBr_2$, no **3b** was detected, though all possible molecules $P_2Br_nI_{4-n}$ could be identified (Table 1). Using *n*Bu_3SnBr or Me_3SnCl instead of $HgBr_2$ left **3a** unreacted while effecting partial replacement of iodide by bromide or chloride in both PI_3 and in P_2I_4. The diphosphorus chloride iodides, $P_2Cl_nI_{4-n}$, were better made by reaction of CS_2 solutions of ICl and P_4 (in molar ratio $\frac{3}{2}:\frac{7}{4}$). Only P_2Cl_3I was not detected (Table 1), while *symm*-P_7I_3 **3a** was a minor product. Neither chlorine-substituted P_7 cage compounds nor iodine-substituted P_4 butterfly compounds were found.

Identification of products by NMR spectroscopy

Ternary halides $P_2X_nY_{4-n}$. Table 1 shows the observed NMR parameters and product distributions of the ternary halides $P_2X_nY_{4-n}$, along with for comparison those of the monophosphorus halides PX_nY_{3-n}. Some molecules in the $P_2Cl_nI_{4-n}$ or $P_2Br_nI_{4-n}$ series have been claimed previously as products of redistribution reactions between P_2I_4 and PCl_3 or PBr_3,[3] but correspondence between our NMR results and those reported, while not ruled out, is not clearly established: in particular, the large splittings due to P—P coupling in the unsymmetrically substituted compounds were not seen in the previous work. Assuming that the spectra were of sufficient quality for reliable observation of such splittings, some factor must have been promoting much more rapid chemical exchange than in the present work, causing collapse and possibly shifting of the multiplets. By briefly reexamining the reac-

Table 1. Relative distribution and NMR parameters of PX_nY_{3-n} and $P_2X_nY_{4-n}$ products

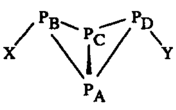
Reaction		[a]			[b]			[c]	
X		Cl			Br			Cl	
Y		Br			I			I	
	mol%	δ	J/Hz	mol%	δ	J/Hz	mol%	δ	J/Hz
PX_3	60	217.4		56	226.1		45	217.5	
PX_2Y	29	222.5		25	219.7		15	225.6	
PXY_2	6.4	225.5		7.4	202.9		8.0	212.1	
PY_3	0.57	226.2		1.4	176.2		9.9	176.1	
P_2X_4	0.18	154.1		0.39	144.3		0		
X_2PPXY	0.75	154.5	−226.8	1.5	148.8	−216.8	0		
		149.7			125.0				
X_2PPY_2	0.57	154.2	−225.2	1.6	149.8	−211.8	0.16	158.5	−215.0
		143.6			96.6			93.3	
XYPPXY (i)	0.42	150.6		0.87	131.0		0.04	143.0	
XYPPXY (ii)	0.42	150.0		1.0	129.7		0.04	139.4	
$XYPPY_2$	1.4	150.1	−223.5	3.5	132.2	−205.9	2.3	141.2	−207.5
		144.3			103.3			103.8	
P_2Y_4	0.48	144.2		1.8	106.3		20	106.3	

[a] $(P_4+Br_2)+Me_3SnCl$.
[b] $(P_4+I_2)+HgBr_2$.
[c] P_4+ICl.

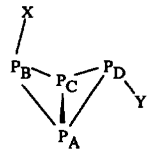
tion between P_2I_4 and PCl_3, we found that this approach to making the mixed P_2X_4 compounds was much more difficult than those now reported, and less likely to give good NMR spectra.

The P—P coupling constants in each mixture of compounds (Table 1) were sufficiently different in value to allow the two multiplets for each unsymmetric molecule to be connected. Their change to more negative values with increasing substitution of more electronegative halide was consistent with trends for the halides α-$P_4S_3X_2$.[5] For both the Cl,Br and Br,I systems all three possible unsymmetric compounds were seen, allowing typical chemical shifts for PX_2, PXY and PY_2 groups to be established. This then allowed the single peaks of the symmetric compounds to be assigned by comparison. The two diastereomers for each formula XYPPXY were of similar relative abundance, and hence presumably of similar stability, so no assignment could be made of which chemical shift belonged to which member.

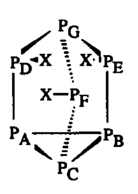
The identification of the mixed diphosphorus tetrahalides according to relative values of chemical shifts and of coupling constants was greatly strengthened by the observation that within a series formed in a particular experiment, the product distribution measured by NMR integration resembled closely the product distribution predicted statistically, assuming labile halogen redistribution. The skewing of the distributions of the diphosphorus tetrahalides to favour molecules containing more of the less electronegative halide, while in the same solution the distributions of the phosphorus trihalides was in the opposite sense, was very noticeable.



1a X = Br, Y = Br
1b X = Br, Y = Cl
1c X = Cl, Y = Cl



2a X = Br, Y = Br
2b X = Br, Y = Cl
2c X = Cl, Y = Br
2d X = Cl, Y = Cl



3a X = I
3b X = Br

Butterfly halides P_4XY. The NMR spectra of the butterfly compounds **1** and **2** were assigned to A_2X_2 or AMX_2 spin systems, giving the chemical shifts and coupling constants shown in Table 2. Besides showing internal consistency, these are quite similar to those for *exo,exo-* or *exo,endo*-$P_4[N(SiMe_3)_2]_2$.[6] The near equality of the two ^1J(P—P) couplings within each of **1b** and **2a–d** caused the multiplets due to bridgehead phosphorus atoms to be unresolved triplets in each case. The splitting due to $^2J(P_BP_D)$ in *exo,exo*-P_4ClBr **1b** was also too small to be resolved.

Signals due to the fully chlorinated compounds **1c** and **2d** could be distinguished on the grounds of increasing relative intensity with increasing relative amount of chloride substitution reagent employed, while the *exo,exo* mixed halide **1b** was distinguishable from the *endo,exo* compounds **2b** and **2c** by showing significantly smaller ^1J couplings. The difference in chemical shift or in coupling constant for the P_B and P_D multiplets of **1b** were the only means of deciding which atom carried chlorine and which bromine, but both these differences were small, so the relative assignment is uncertain.

In **2b** and **2c** the separation of the outer limbs of the triplet due to bridgehead nuclei P_A,P_C corresponded to $J(P_AP_B)+J(P_AP_D)$, which was significantly different in the two compounds. Of the four triplets of doublets due to P_B or P_D in the two compounds, only the two with the largest triplet splittings could be associated with the more widely spaced bridgehead triplet (assigned to **2b**), while only the two with the smallest splittings could correspond to the other (**2c**). Greater broadening of multiplets was observed for phosphorus atoms to which chlorine rather than bromine was attached, resulting from scalar coupling relaxation of ^{31}P by quadrupolar ^{35}Cl or ^{37}Cl. The final decision in assigning structures **2b** or **2c** to the spectra then amounted to deciding which set of multiplets (for all four compounds **2a–2d**) corresponded to phosphorus carrying the *endo* substituent, and which to the *exo*. For this, only chemical shift evidence was available: the negative shifts were more similar to those found for the *exo,exo* compounds, so were assigned to P_D.

In the *exo,exo* compound **1b**, the small value of $^2J(P_BP_D)$ was probably due to cancellation of a positive "through space" contribution from lone pair interaction, by a negative "through bond" contribution. Although we have not yet been able to determine the sign of this coupling in the *endo,exo* molecules, it is therefore probably negative. Change of halide on P_B or P_D will be associated with changes in bond angle to that halogen atom, and with the steric properties of the lone pair of electrons on the phosphorus atom. This in turn would cause a change in bond angles to the opposite halogen, via the through-space P—P interaction. This could explain the differences, similar in magnitude but opposite in sign, in ^1J couplings to P_B or P_D in **1b**, from those for **1a** or **1c**, respectively. Similar "balancing" of deviations in couplings has been observed for compounds α-$P_4S_3(X)Y$.[7,8]

For the *endo,exo* compounds, the nature of the

Table 2. NMR chemical shifts and coupling constants[a] for P_4XY (X, Y = Br or Cl)

	exo,exo-P_4XY			P_4 *endo*-X,*exo*-Y			
	1a	**1b**	**1c**	**2a**	**2b**	**2c**	**2d**
X	Br	Br	Cl	Br	Br	Cl	Cl
Y	Br	Cl	Cl	Br	Cl	Br	Cl
δ_A δ_C	−294.37	−292.05	−290.38	−244.96	−245.84	−234.18	−235.54
δ_B	−72.69	−76.38	−54.46	39.68	14.97	48.77	25.76
δ_D		−74.21		−43.36	−36.87	−43.05	−36.67
${}^1J_{AB}$ ${}^1J_{BC}$	−202.7(3)	−207.9(5)	−215.1(5)	−239.4(4)	−247.0(4)	−240.2(5)	−247.4(4)
${}^1J_{AD}$ ${}^1J_{CD}$		−208.2(4)		−238.7(6)	−245.3(5)	−237.8(7)	−244.3(5)
${}^2J_{BD}$		0.0		±41.9(8)	±38.8(5)	±38.0(9)	±34.6(5)

[a] Chemical shifts are in p.p.m. and coupling constants in Hz with standard deviations (σ) from fitting using NUMARIT (ref. 10) in parentheses.

exo substituent Y appears to control both ${}^1J$ coupling constants and to a considerable extent both chemical shifts $\delta(P_B)$ and $\delta(P_D)$. This may also be attributed to the possibility of cross-ring through space interaction of the lone pair on phosphorus carrying *exo* rather than *endo* substituents. In contrast, the bridgehead chemical shifts $\delta(P_A)$ were controlled mainly by the nature of the *endo* substituent. *Ab initio* MO calculations using GAUSSIAN 92 at the STO-3G level[9] showed that the butterfly skeletal geometry was practically invariant to chloride–bromide substitution, with only the angles to both halogen atoms changing. At the 3-21G* level, *endo,exo*-P_4Cl_2 was found to be marginally more stable, by 0.86 kJ mol^{-1}, than *exo,exo*-P_4Cl_2.

Cage halides P_7X_3. The cage compounds **3a** and **3b** gave NMR multiplets which clearly belonged to a symmetric spin system. This was confirmed by successful computer fitting[10] in both cases to be AA′A″MM′M″X. The resulting NMR parameters are shown in Table 3, which for comparison includes data for the related *symm*-P_7H_3[11] and *symm*-P_7Me_3.[12] Geometries predicted by *ab initio* calculations at the STO-3G level for *symm*-P_7H_3 and for the hypothetical *symm*-P_7Cl_3 were compared with X-ray crystallographic data for *symm*-$P_7(MMe_3)_3$ (M = Si...Pb).[13] Endocyclic angles for the trihydride and trichloride were predicted to be very similar to those measured for the silicon group compounds, which were themselves rather constant. Only the bond angles to the ligands varied notably. These, together with changes in charge distribution (which cannot be predicted reliably at the STO-3G level for such molecules) may be expected to be mainly responsible for the variations in NMR parameters shown in Table 3. Thus, the coupling constants showing the widest variation were those to the phosphorus atoms carrying the

Table 3. NMR chemical shifts and coupling constants[a] for P_7X_3 (X = I, Br, Me and H)

X	I **3a**	Br **3b**	Me[b]	H[c]
δ_A δ_B δ_C	−136.1	−138.8	−154.4	−170.7
δ_D δ_E δ_F	126.0	177.7	65.2	10.7
δ_G	−64.5	−70.7	−91.9	−122.4
${}^1J_{AB}$ ${}^1J_{AC}$ ${}^1J_{BC}$	−221.2(2)	−228.5(1)	−235.1	−220.7
${}^1J_{AD}$ ${}^1J_{BE}$ ${}^1J_{CF}$	−274.0(1)	−284.7(1)	−293.7	−277.1
${}^2J_{AF}$ ${}^2J_{BD}$ ${}^2J_{CE}$	20.9(5)	11.9(1)	31.2	28.6
${}^2J_{AE}$ ${}^2J_{BF}$ ${}^2J_{CD}$	−11.0(5)	−4.9(2)	−9.0	−6.0
${}^2J_{AG}$ ${}^2J_{BG}$ ${}^2J_{CG}$	41.0(1)	40.5(1)	38.3	58.5
${}^1J_{DG}$ ${}^1J_{EG}$ ${}^1J_{FG}$	−323.4(1)	−336.0(1)	−326.6	−261.3
${}^2J_{DE}$ ${}^2J_{DF}$ ${}^2J_{EF}$	−7.7(2)	−5.8(1)	−16.1	−14.8

[a] Chemical shifts are in p.p.m. and coupling constants in Hz with standard deviations (σ) from fitting using NUMARIT (ref. 10) in parentheses.

[b] Ref. 12.

[c] Ref 11.

substituents. The sensitivity of the chemical shifts of these nuclei to the substituent carried was greater than for the butterfly compounds (Table 2) but resembled that for the corresponding molecules α-$P_4S_3X_2$.[5,8]

EXPERIMENTAL

All operations were carried out under nitrogen by Schlenk techniques. P_4, Br_2 and CS_2 were carefully dried. NMR spectra were measured in 10 mm diameter tubes using a Bruker WM300WB spectrometer operating at 121.5 MHz for ^{31}P. Precision capillaries containing $(CD_3)_2CO$ were used for locking, and chemical shifts, obtained by substitution experiments using the same capillaries, are reported relative to H_3PO_4-water.

Typical procedure. A solution of P_4 (0.79 g, 6.4 mmol) in CS_2 (5 cm^3) was stirred vigorously at -10°C while Br_2 (0.16 cm^3, 3.2 mmol) in CS_2 (15 cm^3) was added dropwise over 1 h, to give a pale yellow solution. ^{31}P NMR (2360 scans) showed PBr_3, P_2Br_4 (δ 144.29), *exo,exo*-P_4Br_2 **1a** and *exo,endo*-P_4Br_2 **2a** (Table 2) in molar ratio 95 : 2.7 : 0.48 : 1.9, as well as excess P_4. To a freshly prepared duplicate solution of the phosphorus bromides, Me_3SnCl (1.27 g, 6.4 mmol) in CS_2 (4 cm^3) was added dropwise with stirring over 30 min at 20°C. The volume of solution was reduced to 15 cm^3 by evaporation under vacuum, before sampling for ^{31}P NMR (28000 scans). This showed the distribution of PCl_nBr_{3-n} and $P_2Cl_nBr_{4-n}$ molecules given in Table 1, together with butterfly molecules **1b, 2b** and **2c.** To obtain satisfactory ^{31}P NMR spectra of the P_4Cl_2 molecules **1c** and **2d,** twice the quantity of Me_3SnCl was used.

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