A Stereochemical Study of the Reactions of Trisubstituted Phosphites with *N*-Chlorodialkylamines[1]

Lydia L. Chang and Donald B. Denney*

Wright and Rieman Chemistry Laboratories, Rutgers, The State University of New Jersey, New Brunswick, New Jersey 08903

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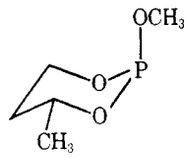
The cyclic phosphites **1** and **2** have been allowed to react with *N*-chlorodialkylamines. Mixtures of geometric isomers of cyclic phosphoramidates result. The loss of stereochemistry is consistent with a mechanism in which there is initial insertion by the phosphorus into the N–Cl bond to give a phosphorane which can pseudorotate in competition with ionization. The results do not eliminate a competing ionic reaction; however, a total ionic process would have been expected to be stereospecific. Rate studies on trivalent phosphorus compounds of varying nucleophilicity show that the rates of the reactions do not follow a straight nucleophilicity order. These results also support the insertion mechanism.

Evidence has been provided that trivalent phosphorus compounds can react with substances containing weak σ bonds to give phosphoranes which are products of insertion into the σ bond. When these products are found in a concerted process, the reaction has been called a "biphilic insertion reaction".[2] The formation of phosphoranes does not in itself yield any information concerning the mechanism of their formation.

In some reactions phosphoranes are formed as unstable intermediates and these decompose under conditions that do not allow for their detection. In these cases indirect methods are required to infer the formation of pentacoordinate intermediates. Two of the more powerful methods for accomplishing this task are stereochemical studies and kinetic investigations.[3]

The stereochemistries of reactions of the two isomeric phosphites **1** and **2** have often been used as a mechanistic



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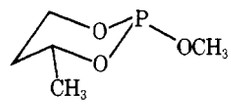

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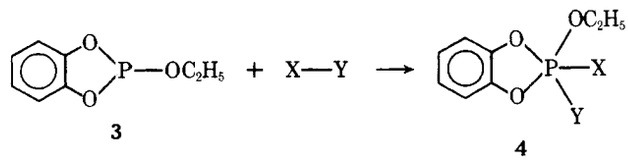
probe. Stereochemically homogeneous reactions have been observed in a number of cases. These results combined with other studies have led to the conclusion that stereochemically pure nonradical reactions follow ionic pathways. They involve as the first step displacement by phosphorus, which is functioning as a nucleophile, to give an ion pair which collapses by attack of the anion of the ion pair on the methyl group carbon. Thus **1** and **2** react stereospecifically with chlorine to give two isomeric phosphorochloridates.[4] Similarly benzenesulfenyl chloride reacts stereospecifically with **1** and **2**.[5] These results have been rationalized in terms of ionic reaction mechanisms. Unfortunately, these results cannot be generalized for all phosphorus containing nucleophiles. For example, it has been recently shown that ethyl catechol phosphite (**3**) reacts at low



3 **4**

X = Y = Cl

X = C_6H_5S; Y = Cl

temperatures with both chlorine and benzenesulfenyl chloride to give phosphoranes. These substances were detected by low temperature ^{31}P NMR measurements.[6] These findings do not eliminate a series of ionic steps for the formation of the phosphoranes; however, direct insertion becomes a viable possibility.

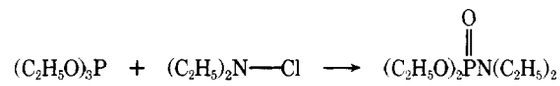
Benzoyl peroxide reacts with **1** and **2** with some loss of stereochemistry.[7] Other work has shown that this is most probably an ionic reaction and that the loss of stereochemistry most likely occurs after the initial displacement.

The reactions of **1** and **2** with neopentyl hypochlorite have been interpreted as involving the formation of pentacoordinate intermediates which undergo permutational isomerization in competition with ionization.[8]

Interpretation of loss of stereochemistry in reactions of **1** and **2** must be done with considerable care. The thermodynamic equilibrium mixture of **1** and **2** is 95:5. Conversion of **2** into the equilibrium mixture is extremely facile and it is catalyzed by traces of acid. Isomerization can compete with the desired reaction and lead to loss of stereochemistry by this pathway.[9] The least stable isomer, **2**, is considerably more nucleophilic than **1** and it is conceivable that the two isomers might react with the same substrate by different reaction mechanisms.

It was the purpose of this work to study the stereochemistries of the reactions of **1** and **2** with various *N*-chlorodialkylamines. At the same time competitive kinetic experiments between various trivalent phosphorus compound were conducted. This was done to assess the response of the rates of the reactions toward variations in the nucleophilicity of the trivalent phosphorus compounds.

Petrov and Sokolskii[10] have studied the reaction of triethyl phosphite with *N*-chlorodiethylamine (**5**). They found that the phosphoramidate, **6**, was the product. More recently

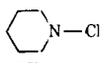
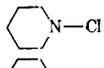
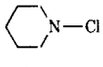


5 **6**

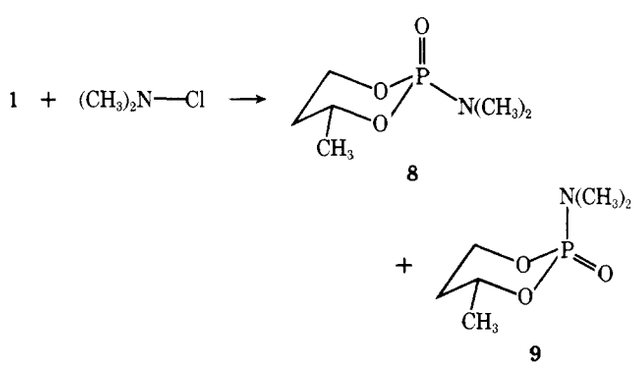
phosphoranes have been isolated from the reactions of *N*-chlorohexafluorodimethylamine with various trivalent phosphorus compounds.[11,12]

There have been two reports of the reactions of **1** and **2** with *N*-chlorodimethylamine (**7**). Mosbo and Verkade[13] allowed **1** to react with **7** in refluxing benzene. They obtained a 2:1 mixture of **8**:**9**. Stec and Mikotajczyk[4] allowed **1** to react with **7** in methylene chloride and they obtained a 91:9 mixture of **8** and **9**. When **2** was allowed to react with **7** a 65:35 mixture of **8** to **9** resulted. The results of these two studies show that the reactions have different stereochemistries and that the stereochemistries are affected by the reaction conditions, i.e., solvent and temperature.

Table I. Reactions of 1 and 2 with *N*-Chlorodialkylamines[a]

Isomer composition, %	R_2NCl	Product composition, %	Solvent	Temp, °C
1:2	$(C_2H_5)_2NCl$	11:12		
95:5	$(C_2H_5)_2NCl$	43:57	Hexane	25
95:5	$(C_2H_5)_2NCl$	65:35	Benzene	25
95:5	$(C_2H_5)_2NCl$	80:20	Benzene	78
95:5	$(C_2H_5)_2NCl$	83:17	Benzene	78
95:5	$(C_2H_5)_2NCl$	22:78	CH_2Cl_2	25
15:85	$(C_2H_5)_2NCl$	80:20	Hexane[b]	25
15:85	$(C_2H_5)_2NCl$	86:14	Benzene	25
15:85	$(C_2H_5)_2NCl$	89:11	Benzene	78
30:70	$(C_2H_5)_2NCl$	84:16	CH_2Cl_2	25
5:95	$(C_2H_5)_2NCl$	95:5	CH_2Cl_2	−70 to 25
1:2	$(CH_3)_2NCl$	8:9		
95:5	$(CH_3)_2NCl$	64:35	CH_2Cl_2	25
5:95	$(CH_3)_2NCl$	48:52	CH_2Cl_2	−78 to 25
5:95	$(CH_3)_2NCl$	45:55	CH_2Cl_2	−78 to 25
5:95	$(CH_3)_2NCl$	49:51	CH_2Cl_2	−78 to 25
95:5	$(CH_3)_2NCl$	40:60	Hexane	25 $t/2$ = 5 h
5:95	$(CH_3)_2NCl$	84:16	Hexane	25 (1 h)
1:2		13:14		
95:5		40:60	CH_2Cl_2	25
10:90		68:32	CH_2Cl	0 to 25

[a] The reactions of the *N*-chlorodiethylamines with 1 and 2, in general, gave the corresponding phosphoramidates in greater than 80% yield. In the reactions of *N*-chlorodimethylamine and *N*-chloropiperidine with 1 and 2, the isomeric phosphoramidates were obtained in 90–95% yield. All isomeric phosphoramidates were identified by ^{31}P NMR peak enhancements with authentic samples prepared via an independent route and by other spectral information. The ratios of the isomers were determined by integration of the ^{31}P NMR spectra on expanded sweep width. In the reactions of *N*-chlorodiethylamine with 1 and 2, the isomer ratios were also determined by the areas obtained by GLC analysis. [b] Run in presence of calcium hydride.



Other reactions of *N*-halo compounds with trivalent phosphorus compounds have been recently reviewed.[14]

Results and Discussion

The percentages of the products of the reactions of 1 and 2 with 7, *N*-chlorodiethylamine (5), and *N*-chloropiperidine (10) are collected in Table I. The products 8 and 9 had been previously characterized.[4,13] The products of the reactions of 5 are 11 and 12 with the same stereochemistries as 8 and 9, respectively. These materials were prepared by an independent route as were 13 and 14, the products of the reaction of 10. The structures of these materials have been assigned on the basis of ^1H and ^{31}P NMR spectroscopy, and on the basis of the effect of a lanthanide shift reagent on the ^1H NMR spectra of these materials. This latter technique has been used previously by Bentrude and Tan[15] and Mosbo and Verkade[13] for similar compounds. The infrared spectra of these compounds followed the pattern observed for similar pairs of isomers.[13,15]

A control experiment was conducted to determine if isomerization of 2 → 1 was important during the reaction of 7 with a 22:78 mixture of 1:2 in methylene chloride. The mixture (2 mmol) was allowed to react with 0.8 mmol of 7. The composition of the remaining starting material after the reaction was 1, 38.5, and 2, 61.5. This change in ratio is due to the greater concentration and reactivity of 2. If rapid isomerization had occurred the ratio would have been 1, 95, and 2, 5. Isomerization is usually fast and complete when it occurs.

The stability of the products was investigated by allowing 1 and 2 to react with 10 in the presence of 14, the least stable isomer. Analysis of the reaction mixture after the reaction showed that the ratio of 13 to 14 was just that which would have been predicted if no isomerization of 14 had occurred.

When *N*-chlorodiisopropylamine (15) was allowed to react with 1 and 2 at 25°C for 2 weeks, there was essentially no reaction. Similarly trimethyl phosphite did not react with 15 over a 2-week period at 25 °C.

The reactions of $(C_2H_5O)_3P$ (16), $C_6H_5P(OC_2H_5)_2$ (17), $(C_6H_5)_2POC_2H_5$ (18), $(C_6H_5)_3P$ (19), methyl ethylene phosphite (20), and methyl catechol phosphite (21) were conducted with pairs of reactants and *N*-chlorodiethylamine. The ratio of products was determined. In each case there was no change in the nature of the products from those obtained from each reactant and *N*-chlorodiethylamine, and also there was no change in the remaining starting materials after the competitive rate studies were completed. The relative rates for the reactions in methylene chloride were found to be $(C_6H_5)_3P$, 3.5; $(C_6H_5)_2POC_2H_5$, 4.5; $C_6H_5P(OC_2H_5)_2$, 3.8; and $(C_2H_5O)_3P$, 1.0. Triethyl phosphite was found to react to the exclusion of 20 which in turn reacted to the exclusion of 21. In hexane the relative rates were $(C_6H_5)_3P$, 2.3; $(C_6H_5)_2POC_2H_5$, 2.1; $C_6H_5P(OC_2H_5)_2$, 2.3; $(C_2H_5O)_3P$, 1.0; 20, 1.0; and 21, 0.11.

The stereochemical results of the reactions of 1 and 2 with the various *N*-chlorodialkylamines show quite clearly that varying amounts of loss of stereochemistry occur during the reactions. The results therefore are suggestive of the formation of phosphoranes as intermediates in the reactions. They do not of course rule out competing ionic reactions and perhaps even changes in mechanism with changes in reaction conditions and reactants. An ionic pathway with 1 as an example and considering displacement on nitrogen as being most likely[14] would be stereospecific as illustrated below.

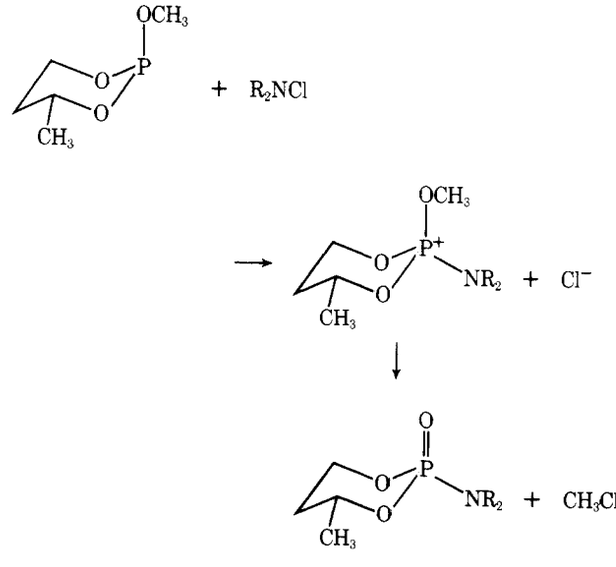


Table II. Spectral Data for 1,3,2-Dioxaphosphorinanes

Registry no.	Compd	R_1	R_2	$\delta^{31}P$, ppm	δ_{CH_3}	δ_{NCH_2}	δ_{NCCH_3}	J_{CHCH_3}	J_{PNCH_2}	$J_{NCH_2CH_3}$	J_{POCCH_3}	IR, cm^{-1} $\nu_{P=O}$ ($CHCl_3$)
54515-66-1		Lone pair	NEt_2	−144	1.22	3.1	1.05	6.5	9.5	7		
54515-67-2		NEt_2	Lone pair	−135	1.28			6.5				
	11	O	NEt_2	−7	1.29	3.08	1.07	6.5	12	7	2.5	1231
	12	NEt_2	O	−3.5	1.38	3.03	1.09	6.5	11	7	1.5	1242
41252-67-9		Lone pair	N	−139.5	1.22	2.7–3.3		6.5				
61062-26-8		N	Lone pair	−134.5								
	13	O	N	−4.5	1.28	2.73–3.3		6.5			2.5	1238
	14	N	O	−2.5	1.37	2.78–3.32		6.5			2.0	1242

Mosbo and Verkade[13] have provided evidence that the most thermodynamically stable isomers of the pair **8** and **9** is **8**, the compound in which the dialkylamino groups is in an equatorial position. The data in Table I show that there is a trend toward this type of product in most cases, the notable exception being the reaction **1**, 95, and **2**, 5, with *N*-chlorodiethylamine in which the opposite was observed. This result was reproducible.

Another anomaly is that Stec and Mikotajczyk[4] found that **1**, 95, and **2**, 5, with **7** gave 91% **8** and 9% **9**. Their results were not duplicated in this study. No apparent reason for these different results can be offered at this time.

The relative rate data suggest that the initial reaction involves insertion into the nitrogen–chlorine bond; however there is an apparent nucleophilic component which renders **20** and **21** less reactive than triethyl phosphite. The opposite reactivity order, i.e., **21** > **20** > **16**, was found for the reaction of diethyl peroxide with these substances.[16] The small rate change with changes in structure in the series **16–19** mimics that found for the diethyl peroxide reaction.[17] It has been shown that in S_N2 displacement reactions the rate increases through the series with triphenylphosphine being the most reactive.[18] Clearly it is not possible to conclude that the stereochemical and kinetic data require the direct insertion mechanism; they do, however, favor it.

Experimental Section

Instrumentation. ^1H NMR spectra were recorded on a Varian T-60 spectrometer. Chemical shifts are reported in parts per million relative to internal tetramethylsilane. Phosphorus NMR spectra were recorded on a Varian HA-100 spectrometer operating at 40.5 MHz and chemical shifts are reported in parts per million relative to external 85% phosphoric acid. Infrared spectra were obtained with a Perkin-Elmer Model 21 spectrometer. GLC analyses were performed on a F and M Model 700 gas chromatograph using a 20 ft × 0.125 in. 5% silicone gum nitrile column, XE-60.

Materials. The trivalent phosphorus compounds were either obtained commercially or prepared by known procedures unless otherwise stated. *N*-Chlorodialkylamines were prepared in hexane, benzene, and methylene chloride by previously reported procedures[19] and they were dried over sodium sulfate. The chloroamine solutions were standardized by iodometric titration. All reactions involving trivalent phosphorus compounds were carried out under an atmosphere of dry nitrogen. The solvents were anhydrous and deoxygenated by a dry nitrogen flush. NMR samples of phosphorus compounds were deoxygenated with a stream of nitrogen. All spectral data are tabulated in Tables II and III.

Preparation of 2-Diethylamino-4-methyl-1,3-dioxaphosphorinane. To a cold (0 °C) solution of 2.93 g (40 mmol) of diethylamine in 50 ml of anhydrous ether was added dropwise with stirring a solution of 3.08 g (20 mmol) of freshly prepared 2-chloro-4-methyl-1,3,2-dioxaphosphorinane in 20 ml of ether. After stirring for 2 h at 0–5 °C the reaction mixture was filtered through a filter stick under nitrogen. The white solid was washed with two 50-ml portions of ether. The combined ether solutions were concentrated to give a colorless oil which gave absorptions at −135 and −144 ppm with approximately equal intensities in the ^{31}P NMR spectrum. Distillation of the mixture at 47–48 °C (0.2 Torr) gave a colorless liquid. Its ^{31}P NMR spectrum showed one absorption at −144 ppm. Upon standing for 5 days, the crude mixture gave one major absorption at −144 ppm (~95%) in the ^{31}P NMR spectrum. This material was assigned the cis configuration.[20]

The ^1H NMR spectrum of a 50:50 mixture of the cis and trans isomers showed two doublets, δ 1.22 (J = 6.5 Hz) and 1.28 (J = 6.5 Hz), for the hydrogens of the ring methyl groups.

Preparation of 2-Diethylamino-4-methyl-2-oxo-1,3,2-dioxaphosphorinane (11). To a chilled solution of 1.91 g (10 mmol) of distilled 2-diethylamino-4-methyl-1,3,2-dioxaphosphorinane in 5 ml of methylene chloride there was added dropwise a saturated solution of N_2O_4 in methylene chloride until a permanent green end point was reached. The excess N_2O_4 and the solvent were removed in vacuo to give 1.8 g (87%) of a yellow liquid, whose ^{31}P NMR shifts were −7 (>95%) and −3.5 ppm (<5%). GLC analysis showed two components in a ratio of 94:6 with retention times of 29 and 46 min. Since the oxidation with N_2O_4 is known to proceed with retention of configuration

this product is assigned the structure **11**. Distillation at 98 °C (0.2 Torr) gave pure **11**.

A mixture of cis and trans isomers (50:50) was oxidized as described above with N_2O_4. The ^{31}P NMR spectrum showed two signals at −7 and −3.5 ppm with approximately equal intensities. GLC analysis showed two components in a ratio of 45:55. Addition of **11** augmented the lower boiling component in GLC analysis and the signal at −7 ppm in the ^{31}P NMR spectrum. The structure of the higher boiling component is assigned as **12**.

Preparation of 2-Piperidinyl-4-methyl-1,3,2-dioxaphosphorinane. This compound was prepared in a manner similar to the methods described above. From 7.7 g (0.05 mol) of 2-chloro-4-methyl-1,3,2-dioxaphosphorinane and 9.4 g (0.11 mol) of piperidine in ether, there was obtained after the usual isolation a colorless liquid. Its ^{31}P NMR spectrum showed two signals at −139.5 (91%) and −134.5 ppm (9%). Distillation at 95–96 °C (1.5 Torr) gave 8.6 g (78%) of a mixture of the cis and trans isomers (91:9).

Preparation of *cis*-2-Piperidinyl-4-methyl-2-oxo-1,3,2-dioxaphosphorinane. The cis isomer was prepared by oxidation of *cis*-2-piperidinyl-4-methyl-1,3,2-dioxaphosphorinane (90:10) with N_2O_4 as described above. Its ^{31}P NMR spectrum showed two signals at −5 (90%) and −2.5 ppm (10%).

Preparation of *trans*-2-Piperidinyl-4-methyl-2-oxo-1,3,2-dioxaphosphorinane (14). A solution of 3.0 g (0.176 mol) of *cis*-2-chloro-4-methyl-2-oxo-1,3,2-dioxaphosphorinane in 30 ml of benzene was added dropwise to a solution of 3.0 g (0.353 mol) of piperidine in 30 ml of benzene with stirring and cooling (5 °C). After the addition, the mixture was stirred at room temperature for 2 h, and the piperidine hydrochloride was removed by filtration. The filtrate was extracted with 50 ml of 1 N hydrochloric acid; it was washed with water and dried over sodium sulfate. Evaporation of the solvent in vacuo gave a light yellow oil which solidified upon standing. Recrystallization of the crude solid from cyclohexane gave 2.5 g (66%) of white, crystalline **14**, mp 59–61 °C.

Reaction of 1 or 2 with *N*-Chlorodialkylamine. A solution of 1.5 g (10 mmol) of **1** or **2** in 10 ml of the chosen solvent was mixed with 8 ml of 1.25 M *N*-chlorodialkylamine in the same solvent at −78 °C. After the mixture was warmed to room temperature, an aliquot was removed for NMR studies which were in turn used to monitor the course of the reaction. After the reaction was completed (less than 0.5 h for **2**, 6 h for **1**), the mixture was concentrated in vacuo and the product distribution was determined by ^{31}P NMR spectroscopy and/or GLC. All components were identified by peak augmentation with an authentic sample. The non-phosphorus-containing byproduct, methyl chloride, was identified by ^1H NMR spectroscopy.

Two control experiments were performed as follows.

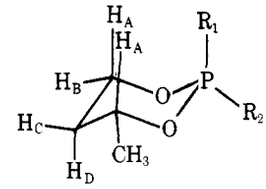
(1) A mixture of 2 mmol of **1** and **2** (22:78) was allowed to react with 0.8 mmol of *N*-chlorodimethylamine. The final mixture contained **1** (0.46 mmol), **2** (0.74 mmol), **8** (0.48 mmol), and **9** (0.35 mmol). The molar ratio of **1** to **2** after reaction is in complete agreement with the calculated based on the assumption that **2** reacts faster than **1** and reacts exclusively with the limiting *N*-chlorodimethylamine. The molar ratio of **8** and **9** was in close agreement with those found in the reaction of **2** with *N*-chlorodimethylamine.

(2) A mixture of 2 mmol of **2** and **1** (73:27) was allowed to react with 1 mmol of *N*-chloropiperidine in the presence of 0.39 mmol of **14**. The final reaction mixture contained nonreacted **2** and **1** in a molar ratio of 42:58 and product **14** and **13** in a molar ratio of 53:47 (0.69 mmol to 0.61 mmol), in addition to 15% of phosphates. After subtracting the amount of **14** present before the reaction, the product ratio of **14** to **13** is 68:32 which is consistent with those found in the reaction of **2** with *N*-chloropiperidine.

Competition Reactions of P(III) Compounds with *N*-Chlorodialkylamines. A solution of 5 mmol of the P(III) compound in 5 ml of solvent (CH_2Cl_2 or hexane) was treated with a solution of 5 mmol of *N*-chlorodiethylamine dropwise at −78 °C with stirring. Usually, there was no reaction at −78 °C; the mixture was then warmed to room temperature and stirred for at least 30 min. ^1H and ^{31}P NMR spectra were recorded before and after the mixture was concentrated.

In competitive rate studies, a solution of *N*-chlorodiethylamine was added dropwise to a solution of a mixture of the two P(III) compounds in a molar ratio of 1:1:1. The product distribution was analyzed by ^{31}P NMR spectroscopy (peak height measurement) and ^1H NMR spectroscopy when feasible.

Table III. Lanthanide[a] Shift Behavior of Selected Protons in 11–14



Compd	Molar[b] ratio	Δδ H_A[c]	Δδ H_B[c]	Δδ $H_{C,D}$[c]
11	0.1	0.23	0.23	0.06
	0.25	1.33	0.8	0.04
	0.5	2.53	0.93	0.9
12	0.1	0.16	0.16	0.28
	0.25	0.40	0.40	0.55
13	0.08	0.44	0.44	0.30
	0.12	1.20	0.20	0.43
	0.19	1.68	0.28	0.58
	0.25	2.10	0.58	0.72,[d] 1.02[e]
14	0.08	0.10	0.10	0.22
	0.12	0.30	0.30	0.25
	0.19	0.41	0.41	0.44
	0.25	0.70	0.70	0.71

[a] Eu(fod)$_3$-d_{30}: tris(1,1,1,2,2,3,3-heptafluoro-4,6-octanedione)europium III-d_{30}. [b] Molar ratio of Eu/P (0.2 M). [c] The downfield shifts in parts per million were obtained by comparing spectra of 0.2 M solution of the phosphorus compounds in $CDCl_3$ with and without added shift reagent. [d] Proton C. [e] Proton D.

Registry No.—**1**, 7735-81-1; **2**, 7735-85-5; **8**, 41158-20-7; **9**, 41158-21-8; **11**, 61062-22-4; **12**, 61062-23-5; **13**, 61062-24-6; **14**, 61062-25-7; chlorodiethylamine, 5775-33-7; chlorodimethylamine, 1585-74-6; *N*-chloropiperidine, 2156-71-0; 2-chloro-4-methyl-1,3,2-dioxaphosphorinane, 6362-87-4; *cis*-2-chloro-4-methyl-2-oxo-1,3,2-dioxaphosphorinane, 38302-69-1.

References and Notes

(1) This work has been supported by the National Science Foundation. This investigation was supported by Grant CA-10737 awarded by the National Cancer Institute, DHEW.
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