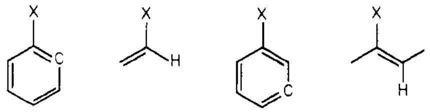
Table V. Comparison of Couplings Involving Carbon in Phenyl Derivatives with those Involving Protons in Vinyl Derivatives



X	J_{CCX}, Hz Obsd	J_{CCX}, Hz Calcd[a]	J_{CCCX}, Hz Obsd	J_{CCCX}, Hz Calcd[a]
H[b]	+1.0	+1.0	+7.4	+7.6
F[c]	+21.0	+ 33.9	+7.7	+21.0
Hg	88	+ 52	102	+118
P	19.5	+4.7	6.7	+12.1

[a] From eq 1 with $a = 0.4$. [b] F. J. Weigert and J. D. Roberts, *J. Amer. Chem. Soc.*, **89**, 2967 (1967). [c] Reference 5a.

Table VI. A Comparison of Vicinal C-X Coupling and Vicinal H-X Coupling in Aliphatic Systems

X	J_{HCCX}, Hz	J_{CCCX}, Hz	X	J_{HCCX}, Hz	J_{CCCX}, Hz
H	7	5	Hg	115	100
P	13	12	F	25	19
P^+	12	15			

are, however, much larger than would be expected from application of eq 1 to the vicinal mercury-proton coupling constants.

While calculating coupling constants involving mercury is impractical, the correlations presented here suggest that if we understand proton-proton coupling, we should at least qualitatively understand carbon-mercury coupling.

Generalizations

The average energy approximation appears to be valid for carbon-carbon couplings but invalid for carbon-fluorine couplings.[10] The magnitudes of the carbon-nitrogen couplings are generally not encouraging for application of eq 2. If we neglect changes in the average energy term, the $^{13}C-^{15}N$ coupling would be predicted to be 0.8 times the carbon-carbon coupling for an analogously hybridized bond. Here we can compare acetylenes (175 Hz)[4] and acetonitrile (17.5 Hz),[3] neopentane (36 Hz)[5c] and the tetramethylammonium ion (5.7 Hz), or benzenes (57 Hz)[5b] and pyridine (0.45 Hz).[15] One-bond carbon-phosphorus couplings in phosphonium ions are also smaller than would be predicted by eq 2. The one-bond coupling constants may be internally consistent with s bond order correlations, but when comparisons are made with carbon-carbon coupling, the failure of the average energy approximation becomes more obvious.

Vicinal coupling in aliphatic compounds is very similar to the corresponding H-X vicinal coupling constants for the limited number of X considered (Table VI). The factors which influence the vicinal coupling for the case X = H have been discussed[16] but no conclusion as to the exact nature of the failure of eq 1 was reached.

Registry No. Methylphosphine, 593-54-4; dimethylphosphine, 676-59-5; trimethylphosphine, 594-09-2; phosphacyclopentane, 3466-00-0; tetramethyldiphosphine, 3676-91-3; triphenylphosphine, 603-35-0; tetrabutylphosphonium bromide, 3115-68-2; methyltributylphosphonium iodide, 1702-42-7; methyltriphenylphosphonium iodide, 2065-66-9; tri-*n*-butyl phosphate, 126-73-8; di-*n*-butyl phosphate, 107-66-4; tri-*n*-propylboron, 1116-61-6; triisopropylboron, 1776-66-5; methyl, 593-74-8; ethyl, 627-44-1; *n*-propyl, 628-85-3; *n*-butyl, 629-35-6; isopropyl, 1071-39-2; vinyl, 1119-20-6; phenyl, 587-85-9.

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(15) R. L. Lichter and J. D. Roberts, *J. Amer. Chem. Soc.*, **93**, 5218 (1971).

(16) G. J. Karabatsos and C. E. Orzech, Jr., *J. Amer. Chem. Soc.*, **87**, 560 (1965).

Contribution from the Departments of Chemistry, University of British Columbia, Vancouver 8, British Columbia, Canada, and The University of Manchester, Manchester 13, England

Reaction of Octafluorocyclotetraphosphonitrile with Methyllithium

T. N. RANGANATHAN,[1a] S. M. TODD,[1b] and N. L. PADDOCK*[1a]

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Octafluorocyclotetraphosphonitrile reacts with methyllithium to give methyl, dimethyl, trimethyl, and tetramethyl derivatives and finally octamethylcyclotetraphosphonitrile. All five dimethyl derivatives were found, and two of them (geminal and trans-antipodal) were characterized completely by ^{31}P, ^1H, and ^{19}F nmr spectroscopy. Trimethylation was exclusively geminal; of the five trimethyl derivatives, the geminal-vicinal and geminal-antipodal compounds have been characterized in detail with the help of their decoupled ^1H and ^{19}F nmr spectra. The single tetramethyl derivative isolated exemplifies a novel orientation pattern in phosphonitrilic chemistry, *viz.*, geminal substitution followed by reaction at an antipodal site. The orientation pattern and the bond length inequalities observed in the structure of *gem*-dimethylhexafluorocyclotetraphosphonitrile are interpreted in terms of perturbation theory applied to a delocalized π-electron system.

Introduction

Very many phosphonitrilic derivatives have been prepared by reactions of chlorophosphonitriles with nucleophiles, and different orientation patterns have been distinguished. At the same time, theories of the π-electron structure of these molecules have been developed and have been used for the interpretation of molecular structure and energetics, though there has hitherto been no systematic attempt to apply the theory to strictly chemical problems, such as the orientation of substituents or the rates of the reactions by which they are introduced. This is partly because reactivity is not a

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(1) (a) University of British Columbia. (b) University of Manchester.

simple ground-state property and partly because the high polarity of the P–N bond allows many substitutional effects to be interpreted in terms of polar effects; for some purposes, the electronic behavior of a substituent is sufficiently expressed by the terms "electron releasing" or "electron withdrawing," successive nucleophilic substitution at the same phosphorus atom being thereby retarded or accelerated. Such a simple view is adequate for explaining the geminal orientation pattern in the fluorination of the cyclic phosphonitrilic chlorides[2] and the predominantly nongeminal pattern of their dimethylamination,[3] but the details, especially the relative rates of reaction, require consideration of π-electron effects.[2] The arylation of hexafluorocyclotriphosphonitrile by phenyllithium proceeds both geminally and nongeminally,[4] the smaller importance of the former orientation pattern being attributed to steric inhibition by the first entering phenyl group. That such interactions can be important is seen particularly clearly in the structure of *cis*-$(NPPhCl)_4$, in which the eight-membered ring has a crown conformation,[5] which is not expected and not found in homogeneously substituted phosphonitriles but which uniquely provides more space on one side of the molecule for the phenyl groups than for the chlorine atoms on the other. It is clear that steric interactions can affect molecular properties and presumably reactivity.

In the present investigation, we have studied the methylation of $(NPF_2)_4$ with methyllithium, to simplify and to elucidate in more detail the factors affecting substitution. The steric requirements of the methyl group are not extreme, and its conjugative effect, in contrast to those found in phenylation and dimethylamination reactions, is expected to be small, though perhaps not negligible. Its influence is expected to be felt mainly through direct-field, σ-inductive, and π-inductive interaction. The first two are difficult to distinguish from each other; the third represents those effects of a substituent on the π-electron distribution which involve no net charge migration between the ring and the substituent and is an important concern of the present work. It is appropriately investigated through reactions of the phosphonitrilic fluorides, because $p\pi$–$d\pi$ bonding is expected to be strongest in these molecules. The contribution of the d orbitals depends on their contraction by electronegative ligands and is maximized in the fluorophosphonitriles, as shown by such properties as the molecular structure of $N_4P_4F_8$[6] and the ionization potentials of the series $(NPF_2)_n$,[7] the latter measurements, especially, making clear the effects of both ligand electronegativity and ring size. The structural information discussed in the paper shows that the effect of a methyl group extends through four bonds, and a unified explanation of the bond length inequalities and the orientation pattern is possible in terms of simple perturbation theory applied to a cyclically delocalized π system.

Experimental Part

Octafluorocyclotetraphosphonitrile, $N_4P_4F_8$, was prepared from the chloride by reaction with an excess of potassium fluorosulfite in paraffin at 120°. It was freed from sulfur dioxide on a vacuum line and further purified by distillation *in vacuo*. Methyllithium was prepared by adding methyl bromide (usually 30–50% in excess of theory) in diethyl ether in small portions to a weighed quantity of lithium ribbon of high quality in ether, the reaction mixture being stirred in a nitrogen atmosphere for 2 hr, when all the lithium had dissolved. The excess of methyl bromide was removed by heating under reflux for 30 min. The experimental method used was essentially the same for all preparations and is described in detail only for $N_4P_4F_7Me$, below. The products of reaction were separated partly by fractional distillation (spinning-band column) and partly by gas–liquid chromatography (Varian A90P, column 10 ft × $^1/_4$ in., 20% Carbowax 20M on Chromosorb W, 60–80 mesh, treated with HMDS). The pure compounds were characterized by analysis and by high-resolution mass spectrometry (MS9 mass spectrometer). ^1H, ^{19}F, and ^{31}P nmr spectra were obtained on a Varian HA100 instrument, with heteronuclear decoupling where necessary. Infrared spectra of dilute solutions of all the compounds in carbon disulfide and in carbon tetrachloride were recorded on a Perkin-Elmer spectrophotometer, Model 457, as well as spectra of thin films (liquids) or Nujol mulls (solids), and Raman spectra were recorded on a Cary 81 spectrometer equipped with a Spectra-Physics 125 laser source. Liquids were studied as such and the solids as powders or solutions in chloroform, benzene, or carbon tetrachloride.

Methylheptafluorocyclotetraphosphonitrile. Methyllithium (25.6 mmol) in 50 ml of diethyl ether was added dropwise to octafluorocyclotetraphosphonitrile $N_4P_4F_8$ (7.7 g, 23.2 mmol) in 60 ml of ether at −20°, under nitrogen. The addition was complete in 2 hr, the temperature then being allowed to rise, and the reaction was continued for a further 10 hr at room temperature. The solution was filtered from lithium salts under nitrogen pressure and distilled. Unreacted $N_4P_4F_8$ (1.8 g, 5.4 mmol) was recovered from the ether. The crude product (3.7 g) on fractional distillation gave 3.1 g of a clear liquid, which was purified chromatographically (100°, 40 cm^3 of He/min) to give methylheptafluorocyclotetraphosphonitrile, bp 130.7° (756 mm). *Anal.* Calcd for $CH_3F_7N_4P_4$: C, 3.9; H, 1.0; F, 40.6; N, 16.9. Found: C, 3.7; H, 0.9; F, 40.6; N, 17.1. Mass: calcd, 327.919; measd, 327.918. A smaller fraction (0.4 g, bp 100–110° (100 mm)) consisted mainly of isomers of $Me_2F_6N_4P_4$.

Dimethylhexafluorocyclotetraphosphonitriles and Trimethylpentafluorocyclotetraphosphonitriles. In another, otherwise similar experiment, a larger proportion of the dimethyl derivatives was obtained by increasing the amount of methyllithium. Distillation of the product (6.4 g) of the reaction between octafluorocyclotetraphosphonitrile (8.5 g, 25.6 mmol) and methyllithium (69.9 mmol) in 75 ml of diethyl ether gave 1.9 g (5.8 mmol) of $N_4P_4F_7Me$ and 3.8 g of a clear liquid, bp 85–95° (30 mm)). On further fractionation by glc, two sets of incompletely separated compounds were obtained, the first set (liquid, 3.0 g) being a mixture of isomers of $N_4P_4F_6Me_2$ and the second set (low-melting solid, 0.8 g) being a mixture of isomers of $N_4P_4F_5Me_3$. In a third experiment, 6.8 g of crude product from the reaction of $N_4P_4F_8$ (10 g, 30.1 mmol) with methyllithium (100.1 mmol) in 160 ml of ether gave 0.5 g (1.5 mmol) of $N_4P_4F_7Me$, 1.4 g (4.4 mmol) of a mixture of isomers of $N_4P_4F_6Me_2$, 3.4 g (10.6 mmol) of a mixture of isomers of $N_4P_4F_5Me_3$, and a residue (0.8 g) containing further isomers of $N_4P_4F_5Me_3$, from all of which a solid (0.2 g) separated, subsequently identified as $N_4P_4F_4Me_4$ (see below).

The two mixtures of $N_4P_4F_6Me_2$ were fractionated further by glc and found to have approximately the same isomer composition. They were mixed and separated chromatographically (90°, 30 cm^3 of He/min) into four components, their proportions being as follows: 1, 40.7%; 2, 11.2%; 3, 16.3%; 4, 31.8%. Component 4 was partly resolved into two on a longer (20-ft) column, the separation being good enough to show the presence of all five possible isomers of $N_4P_4F_6Me_2$ in the original mixture. **Component 1** (mp 49.5°) was identified by its nmr spectra as the gem isomer. *Anal.* Calcd for $C_2H_6F_6N_4P_4$: C, 7.4; H, 1.9; N, 17.3. Found: C, 7.4; H, 1.7; N, 17.1. Mass: calcd, 323.944; measd, 323.942. **Component 2** was shown by its nmr spectra to be a nongeminal isomer but was not further characterized. *Anal.* Found: C, 7.4; H, 1.9. **Component 3** (mp 70–71°) was identified through its nmr spectra as trans-antipodal $N_4P_4F_6Me_2$. *Anal.* Found: C, 7.2; H, 1.9; mass measd 323.945. **Component 4** (two-compound mixture) was analyzed. *Anal.* Found: C, 7.2; H, 2.0; N, 17.1. The mixture of isomers of $N_4P_4F_5Me_3$ was separated chromatographically into two compounds, the first being 1,1,3-trimethylpentafluorocyclotetraphosphonitrile, mp 29.5°, **component 5**. *Anal.* Calcd for $C_3H_9F_5N_4P_4$: C, 11.3; H, 2.8; F, 29.7; N, 17.5. Found: C, 11.4; H, 3.0; F, 29.4; N, 17.4. Mass: calcd, 319.969; measd, 319.970. The second isomer, **component 6**, mp, 70.2°, was 1,1,5-trimethylpentafluorocyclotetraphosphonitrile. *Anal.* Found: C, 11.3; H, 2.9; F, 29.5; N, 17.4; mass measd 319.970. The two isomers were formed in the ratio 3:4.

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(2) J. Emsley and N. L. Paddock, *J. Chem. Soc. A*, 2590 (1968).

(3) M. Becke-Goehring, K. John, and E. Fluck, *Z. Anorg. Allgem. Chem.*, 302, 103 (1959); S. K. Ray and R. A. Shaw, *J. Chem. Soc.*, 872 (1961).

(4) C. W. Allen and T. Moeller, *Inorg. Chem.*, 7, 2177 (1968).

(5) G. J. Bullen and P. A. Tucker, *Chem. Commun.*, 815 (1970).

(6) H. McD. McGeachin and F. R. Tromans, *J. Chem. Soc.*, 4777 (1961).

(7) G. R. Branton, C. E. Brion, D. C. Frost, K. A. R. Mitchell, and N. L. Paddock, *J. Chem. Soc. A*, 151 (1970).

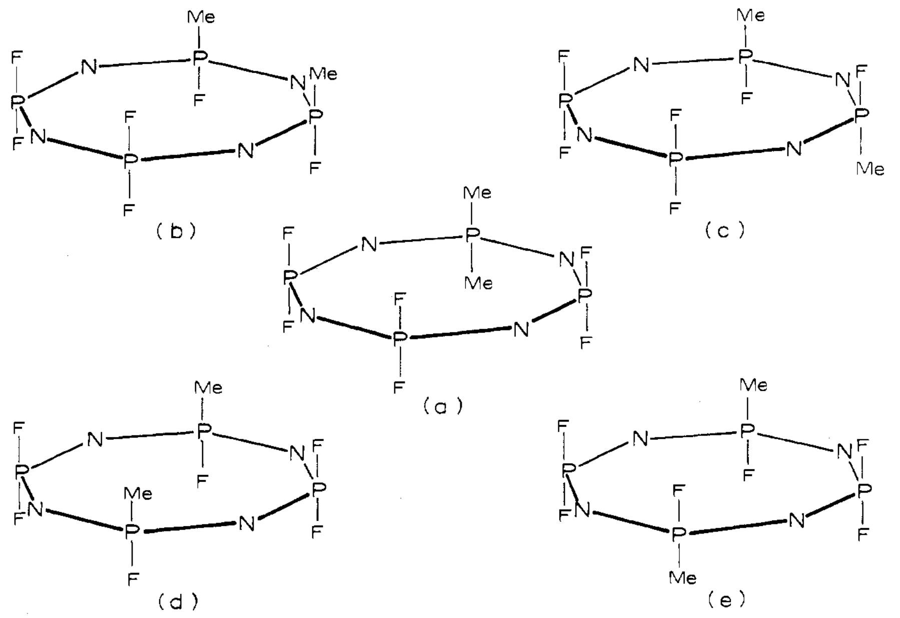

Figure 1. Isomers of $N_4P_4F_6Me_2$. b and c are vicinally and d and e are antipodally substituted.

Tetramethyltetrafluorocyclotetraphosphonitrile. After completion (12 hr) of the reaction of $N_4P_4F_8$ (7.2 g, 21.6 mmol) with methyllithium (81.6 mmol) in 150 ml of diethyl ether at −20°, the solvent was distilled off, and the residue was extracted with petroleum ether. The crude product (5.1 g) was a mixture of solid and liquid, largely dimethyl and trimethyl derivatives, from which a crystalline solid (1.6 g), mp 171–172°, was obtained by sublimation. It was shown chromatographically to be a single compound and identified through its nmr spectra as 1,1,5,5-tetramethyltetrafluorocyclotetraphosphonitrile. *Anal.* Calcd for $C_4H_{12}F_4N_4P_4$: C, 15.2; H, 3.8; F, 24.1; N, 17.8. Found: C, 15.4; H, 3.9; F, 24.0; N, 18.0. Mass: calcd, 315.994; measd, 315.944.

Octamethylcyclotetraphosphonitrile. In a similar reaction, 243 mmol of methyllithium reacted with 9.1 g (27.5 mmol) of $N_4P_4F_8$ in 150 ml of ether at −20° to give 7.0 g of material soluble in chloroform. The solid was purified by sublimation *in vacuo* and by recrystallization from petroleum ether to give octamethylcyclotetraphosphonitrile (5.2 g, theory 63.2%; mp 162–163°, lit.[8] mp 162–164°).

Structures

Most structures were established by nmr spectroscopy, vibrational spectroscopy providing important additional information in some cases. The ^1H nmr spectra were interpretable in terms of a first-order treatment, but the ^{19}F and ^{31}P spectra all showed second-order effects, which diminished as the degree of methylation increased. In most cases, decoupling led to unequivocal structural assignments. Positional and stereo isomers were identified, but there was no evidence of conformational isomerism. All the nmr results could be interpreted on the basis of a statistically planar ring. Chemical shifts are quoted relative to internal tetramethylsilane, internal $CFCl_3$, and external P_4O_6.

Nuclear Magnetic Resonance Spectra. Methylheptafluorocyclotetraphosphonitrile. In $N_4P_4F_7Me$, the single ^{31}P resonance in $N_4P_4F_8$ (δ^P 129.7 ppm, J_{PF} = 836 Hz (from ^{19}F spectrum)) is split into a high-field triplet (PF_2, δ^P 125.2 ppm, J_{PF} = 861 Hz) and a low-field doublet (PFMe, δ^P 86.7 ppm, J_{PF} = 939 Hz) in the ratio 3:1. The ^{19}F spectrum consists of two doublets in the ratio 6:1 (PF_2, δ^F 69.7 ppm, J_{PF} = 866 Hz; PFMe, δ^F 57.6 ppm, J_{PF} = 942 Hz). The PF_2 part of the spectrum is complicated by second-order effects. The interpretation of the ^1H spectrum is straightforward; the main doublet (τ 8.30, J_{CH_3P} = 18.7 Hz) arising from coupling of the protons of the methyl group with the phosphorus to which it is directly bonded is split further by coupling with the unique fluorine atom (J_{CH_3F} = 6.5 Hz), and each component is then split into incompletely resolved 1:2:1 triplets by interaction with vicinal phosphorus atoms (J'_{CH_3P} = 1.5 Hz).

Dimethyl Derivatives. Component 1 was identified as the gem isomer (Figure 1a) by its ^{31}P nmr spectrum which consists of a 1:2:1 triplet (PF_2, δ^P 126.5 ppm) and a singlet (PMe_2, δ^P 93.0 ppm). The PF_2 groups are further distinguishable in the ^{19}F spectrum, which consists of two doublets of relative area 1:2 (δ^F 69.2 ppm, J'_{PF} = 845 Hz; δ^F 68.5 ppm, J'_{PF} = 846 Hz). Both doublets have unresolved fine structure. The ^1H spectrum consists of six lines, each component of the main doublet (τ 8.36, J'_{CH_3P} = 14.6 Hz) being split into triplets by coupling of the methyl protons with the vicinal phosphorus atoms (J'_{CH_3P} = 1.4 Hz). The geminal structure has been confirmed crystallographically.[9] No ^{31}P nmr spectrum was obtained for component 2, and the PF_2 region of the ^{19}F spectrum was found to be too complicated for first-order interpretation. The nongeminal nature of this isomer is indicated by the lower field region (PFMe, δ^F 55.3 ppm, J'_{PF} = 981.4 Hz) and by the ^1H spectrum (τ 8.28, J'_{CH_3P} = 18.5 Hz, J'_{CH_3F} = 5.3 Hz), but the detailed position of the methyl groups was not established. The main doublet in the ^1H spectrum of component 3 is similar (τ 8.37, J'_{CH_3P} = 18.8 Hz, J'_{CH_3F} = 6.3 Hz) but is split further by interaction with the vicinal phosphorus atoms (J'_{CH_3P} = 1.7 Hz). The resulting pattern of four triplets would be expected for either of the antipodally substituted isomers (Figure 1d, e) or (since the coupling of second-nearest neighbors is weak) the two vicinally substituted isomers (Figure 1b, c). The structure of the compound is established as *trans*-1,5-dimethyl-1,3,3,5,7,7-hexafluorocyclotetraphosphonitrile (Figure 1e) by its ^{19}F nmr spectrum, which consists of two doublets of relative area 2:1 (PF_2, δ^F 69.6 ppm, J'_{PF} = 872 Hz; PFMe, δ^F 56.6 ppm, J'_{PF} = 946 Hz). If the compound had a vicinal or cis-antipodal structure, the fluorine atoms in each

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[8] H. T. Searle, *Proc. Chem. Soc., London*, 7 (1959).

[9] W. C. Marsh, T. N. Ranganathan, J. Trotter, and N. L. Paddock, *Chem. Commun.*, 815 (1970); W. C. Marsh and J. Trotter, *J. Chem. Soc. A*, 573 (1971).

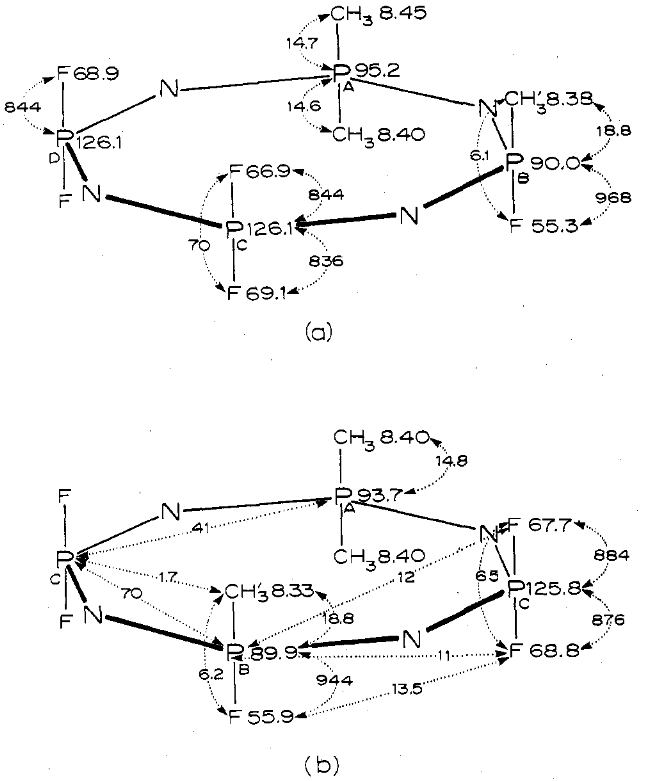

Figure 2. Chemical shifts and coupling constants of (a) 1,1,3-trimethylpentafluorocyclotetraphosphonitrile and (b) 1,1,5-trimethylpentafluorocyclotetraphosphonitrile.

PF_2 group would be magnetically inequivalent. Geminal coupling constants J_{FF} in these circumstances have been found[4] to be about 70 Hz in 1,3-$N_3P_3F_4Ph_2$ and 1,1,3-$N_3P_3F_3Ph_3$, and similar values are found (below) in the trimethylpentafluorocyclotetraphosphonitrile derivatives. No sign of the splitting was found, so that component 3 is assigned the trans-antipodal structure. The incompletely separable mixture, component 4, had a ^1H nmr spectrum consisting of a doublet of doublets arising from PFMe groups (τ 8.28, J'_{CH_3P} = 18.2 Hz, J'_{CH_3F} = 5.8 Hz). No further clarification was obtained by irradiation at either the ^{31}P or the ^{19}F spectrum, the PFMe region consisting of two doublets (δ^F 55.8 ppm, J'_{PF} = 962 Hz; δ^F 56.9 ppm, J'_{PF} = 946 Hz) but the PF_2 region is too complicated for interpretation, and detailed structures are not assigned.

Trimethyl Derivatives. Heteronuclear decoupling techniques were found to be essential for the elucidation of the nmr spectra of the trimethyl derivatives; deduced values of shifts and coupling constants are shown in Figure 2.

The presence of PF_2, PFMe, and PMe_2 groups in component 5 is shown by its ^{31}P nmr spectrum, which consists of a high-field triplet (PF_2), a singlet (PMe_2), and a low-field doublet (PFMe), so ruling out the three nongeminal structures. The geminal-vicinal structure (Figure 2a) is established by the ^{19}F nmr spectrum, in which the PF_2 groups are distinguishable. The ^1H nmr spectrum is complex (Figure 3a) but is simplified by heteronuclear decoupling. The spectrum (Figure 3b) obtained on irradiating at the ^{19}F resonance frequency (94.089650 MHz) consists of three doublets, the two methyl groups in the PMe_2 group being differentiated by the vicinal PFMe group, itself identified by its coupling constant. Irradiation at the ^{31}P resonance frequency (40.481330 MHz) (Figure 3c) leaves only the ^{19}F coupling, and the three methyl environments are clearly apparent. The assignment of the two proton shifts (Figure 2a) of the PMe_2 group is arbitrary and (with the assignments of the coupling constants) could be reversed. The ^{19}F nmr spectrum is compatible with the same structure. A first-order treatment is applicable, the two fluorine atoms on P_C (but not on P_D) being inequivalent. $J_{FF}(P_CF_2)$ is similar to previously reported values.[4] The assignments of the ^{19}F chemical shifts and coupling constants of the same group are made on the basis of an indirect argument about coupling constants (see the following section). They could be reversed without altering the structural assignment of the compound as 1,1,3-trimethyl-3,5,5,7,7-pentafluorocyclotetraphosphonitrile. **Component 6** is more symmetrical, and its spectra are more informative in detail (Figure 2b). The ^{31}P nmr spectrum (solution in CCl_4) consists of a low-field doublet, a broad singlet, and a 1:2:1 triplet, arising from PFMe, PMe_2, and PF_2 groups. The doublet and the singlet are complex, owing to long-range coupling, but the triplet is relatively simple, each component being split by P_A and P_B into a doublet of doublets. The normal ^1H nmr spectrum is complex (Figure 3d), but irradiation at the ^{19}F resonance frequency (94.088880 MHz) allows the confirmation of the presence of a PFMe and PMe_2 group (Figure 3e). Irradiation at the ^{31}P resonance frequency (40.481330 MHz) leaves the ^{19}F coupling (Figure 3f); the resonance signals of the methyl protons in the PMe_2 group are broad in the decoupled spectra, suggesting slight inequivalence of the two methyl groups. The detailed structure is proved by the ^{19}F nmr spectrum, the number and positions of the lines being interpretable on a first-order basis, though their relative intensities are only approximately correct. The two PF_2 groups are found to be equivalent to one another, though the two fluorine atoms in the same group are not. The coupling $^4J_{FF}$ between fluorine atoms on adjacent phosphorus atoms has been observed (for the first time) as 13.5 Hz; in cyclohexane and carbohydrate chemistry $^4J_{FF}(cis) > {}^4J_{FF}(trans)$,[10] and we assume, tentatively, that the same is true here, the assignment of the shifts and coupling constants of the PF_2 groups being based on the assumption that only $^4J_{FF}(cis)$ is observed. Reversal of this assignment would leave the structural assignment of the compound as 1,1,5-trimethyl-3,3,5,7,7-pentafluorocyclotetraphosphonitrile unchanged.

Tetramethyltetrafluorocyclotetraphosphonitrile. The ^{19}F nmr spectrum of this compound consists of a doublet of triplets; the absence of a low-field doublet shows the absence of PFMe groups, all groups being geminal. The ^1H nmr spectrum is also a doublet of triplets, indicating a geminal-antipodal structure, though the geminal-vicinal structure cannot be ruled out on this basis, because the coupling constants might be insufficiently different to allow a distinction to be made between a triplet and a doublet of doublets. The ^{31}P nmr spectrum is uniquely consistent with the geminal-antipodal structure (Figure 4). It consists of a triplet of triplets and a broad singlet; for the geminal-vicinal structure a triplet of doublets (six lines) would be expected. The structural assignment as 1,1,5,5-tetramethyl-3,3,7,7-tetrafluorocyclotetraphosphonitrile has been confirmed crystallographically.[9,11] Chemical shifts and coupling constants are shown in Figure 4.

Octamethylcyclotetraphosphonitrile. The ^1H nmr spectrum (solution in CCl_4) consists of a doublet (τ 8.66, J_{CH_3P} = 12.0 Hz) with an unsymmetrical shoulder on each component; the coupling of methyl protons with vicinal protons is not re-

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(10) L. D. Hall, personal communication; R. J. Abraham, *J. Chem. Soc. B*, 1022 (1969).

(11) W. C. Marsh and J. Trotter, *J. Chem. Soc. A*, 569 (1971).

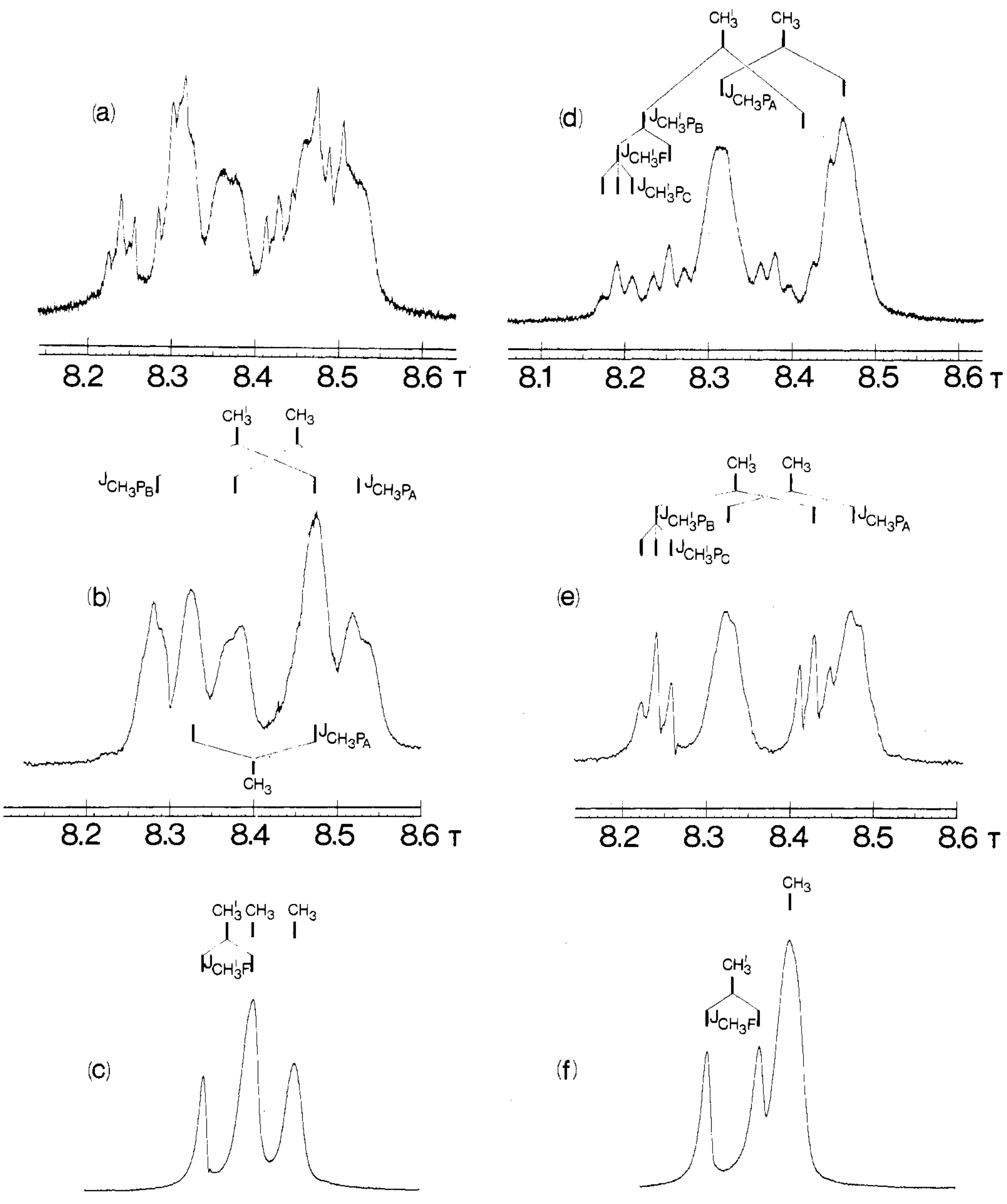

Figure 3. Direct (a) and decoupled (b, ^{19}F; c, ^{31}P) proton spectra of 1,1,3-trimethylpentafluorocyclotetraphosphonitrile. Comparable information for the 1,1,5 isomer is given by d, e, and f.

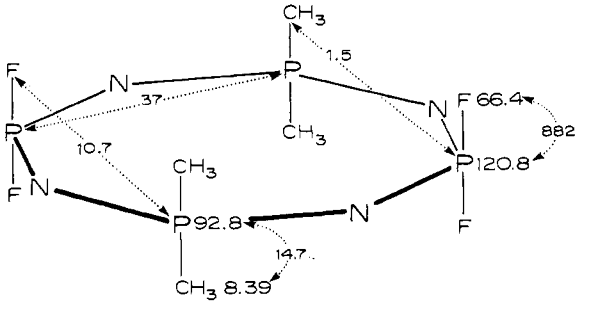

Figure 4. Chemical shifts and coupling constants of 1,1,5,5-tetramethyl-3,3,7,7-tetrafluorocyclotetraphosphonitrile.

solved either here or in the ^{31}P spectrum (δ^P 98.7 ppm (CCl_4), 86.2 ppm (D_2O)).

Vibrational Spectra. The vibrational spectra of the phosphonitrilic halides have received considerable recent attention, and frequency assignments of most fundamentals have been suggested. While many assignments for the present series of compounds are possible, especially because of the general similarity of the spectra of the monosubstituted derivatives $N_4P_4F_7X$ (X = NMe_2, Cl, Br, NCS, Me), the lower frequency ring modes, in particular, require a fuller discussion than can be given here, and the detailed treatment, which will be published later, does not add significantly to the conclusions derived from the nmr spectra. Attention is here restricted to the vibrations of the methyl group and the strong ν_{as} (PNP) vibration. Numerical values are given in Table I.

Discussion

In broad outline, the reaction of methyllithium with octafluorocyclotetraphosphonitrile takes place as shown in Figure 5. Its noteworthy features are that (1) although all five dimethyl derivatives are produced, the geminal isomer is the most abundant (40% of the dimethyl derivatives), (2) no non-

Table I. Selected Vibrational Frequencies (cm^{-1}) of Methyl Fluorophosphonitriles[a]

Compd	ν_{as}(CH)[b,c]	ν_s(CH)[d]	$\delta_{as}(CH_3)$[c]	$\delta_s(CH_3)$[e]	ν_{as}(PNP)[f]
$MeN_4P_4F_7$	3018	2938	*g*	1315	1410
1,1-$Me_2N_4P_4F_6$	3004	2938	*g*	1304[h]	1390
1,5-$Me_2N_4P_4F_6$	3005	2932	*g*	1315[h]	1386
1,1,3-$Me_3N_4P_4F_5$	3000	2935	*g*	1311, 1302	1375
1,1,5-$Me_3N_4P_4F_5$	3003	2935	*g*	1314, 1307	1372
1,1,5,5-$Me_4N_4P_4F_4$	3001	2930	1425, 1414	1310, 1303	1355
$Me_8N_4P_4$	2995	2931	1422/1430, 1415	1302, 1285	1221
$MePF_2$[i]	2987	2910	1410	1287	
$MeNH_2$[j]	2962	2842, 2833[k]	1460	1410	

[a] From infrared spectra, dilute solution in CS_2 and/or CCl_4. [b] Where measured, the Raman line is depolarized. [c] Ir intensity relative to symmetric vibration increases with methyl substitution. [d] Where measured, the Raman line is polarized. [e] Absent in Raman. [f] ν_{as}(PNP) in $N_4P_4F_8$ is 1410/1435 cm^{-1}. [g] Obscured by ν_{as}(PNP). [h] Second band not detected with certainty; possibility of confusion with ring vibrations. [i] F. Seel, K. Rudolph, and R. Budenz, *Z. Anorg. Allgem. Chem.*, **341**, 196 (1965). [j] J. R. B. Matutano and J. Bellanato, *Spectrochim. Acta*, **8**, 27 (1956). [k] Resolution of degeneracy.

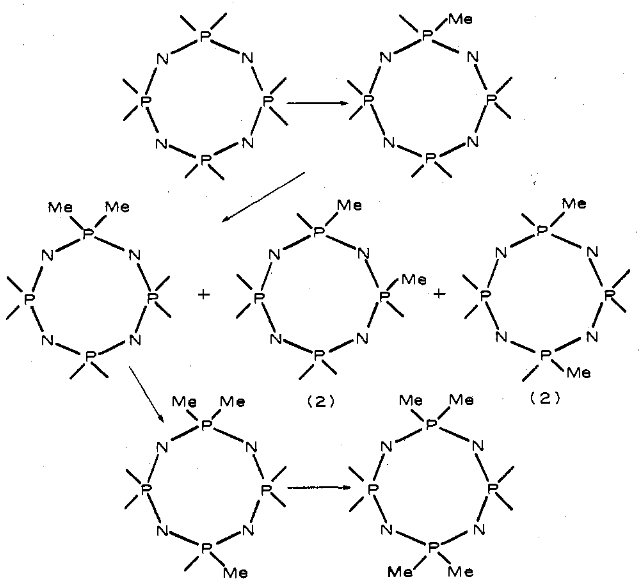

Figure 5. The principal orientation pattern observed in the reaction of octafluorocyclotetraphosphonitrile with methyllithium. Fluorine atoms are not shown.

geminal tri- or tetramethyl derivatives have been found, and (3) the preferred reaction site of the third methyl group is antipodal to the first two.

In order to understand these features, which are believed to have a common basis, it is useful to consider the substitution reactions of phosphonitrilic compounds more generally.

The extent to which alternative products are formed may depend on their relative thermodynamic stabilities or on the nature of the substrate molecule itself, the solvent, or the attacking reagent. In the present work, the solvent and reagent are constant, and the possible effects of the electron distribution in the substrate molecule on reactivity are considered first. The rate of nucleophilic displacement of a chloride ion from a phosphonitrilic chloride is usually increased by an electron-withdrawing group, such as fluorine,[2] and decreased by an electron-releasing amino group.[12] I_σ effects can account for the nongeminal antipodal amination of $N_4P_4Cl_8$[13] and for its geminal-vicinal fluorination by KSO_2F[2] but not for the predominantly geminal substitution of $N_3P_3Cl_6$ by aniline[14] or the relative rates of the first and second steps in the fluorination of $N_3P_3Cl_6$ and $N_4P_4Cl_8$.[2] Further, on a purely electrostatic basis, all substitution reactions of the phosphonitrilic fluorides should give nongeminal products. The pattern of methylation described here shows not only that geminal substitution can be dominant but also that a third substituent can enter antipodally to the first two, a novel orientation pattern, inexplicable in electrostatic terms.

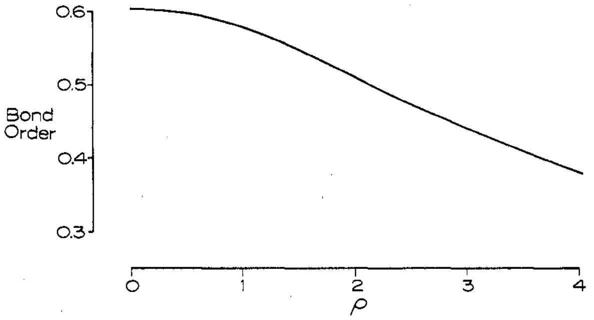

Figure 6. Bond order of the N_4P_4 ring as a function of the relative electronegativity of P and N; $\rho = (\alpha_N - \alpha_P)/\beta$.

These features are explicable if the effect of a first substituent on the π-electron distribution is included. Conjugative interactions are involved in the amination reactions, and their consideration is deferred; they are expected to be minimal with the methyl group, whose interactions are mainly of the π-inductive type. The internal vibrations of the methyl group are insensitive to the degree of substitution, and comparison of the mean values with those of $MePF_2$, $MeNH_2$, and other methyl derivatives[15] shows that the frequencies are approximately characteristic of attachment to pentavalent phosphorus and there is no major effect of the ring upon them.

In contrast, ν_{as}(PNP) is much more sensitive to substitution, decreasing by approximately 200 cm^{-1} from $N_4P_4F_8$ to $N_4P_4Me_8$. The mean P-N bond lengths (Å) also decrease in the following series: $N_4P_4F_8$, 1.510;[6] 1,1-$N_4P_4F_6Me_2$, 1.518;[9] 1,1,5,5-$N_4P_4F_4Me_4$, 1.562;[11] $N_4P_4Me_8$, 1.595.[16] The methyl groups evidently weaken the ring bonds, without themselves being greatly affected. This is as expected for π-inductive interactions, the methyl group reducing the electronegativity of the phosphorus atom to which it is attached. Figure 6 shows how the calculated bond orders, on the Huckel model, decrease with increasing ρ, the relative electronegativity of nitrogen and phosphorus. The variation is parallel to that of ν_{as}(PNP) and the mean bond length with increasing methylation.

The same model is useful for correlating the deviations from

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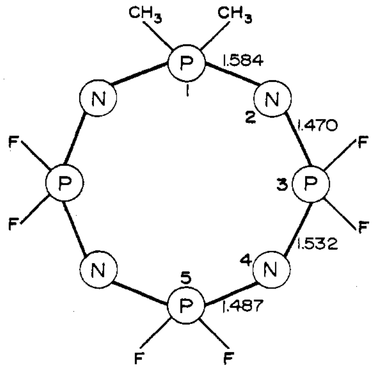

Figure 7. Idealized structure and PN bond lengths in *gem*-$N_4P_4Me_2F_6$ (σ(P-N) = 0.006 Å).[9]

mean bond length induced by a substituent. Figure 7 shows the structure of *gem*-$N_4P_4F_6Me_2$.[9] The ring has a saddle shape, but the mean deviation of the nitrogen atoms from the plane of the phosphorus atoms is small enough (0.15 Å) for the ring to be considered substantially planar. The longest bond (from the Me_2P group) is followed by the shortest P-N bond in the molecule, the third bond being intermediate in length between the first two and the fourth being intermediate between the second and the third. This bond alternation is not explicable in terms of σ-inductive or direct-field effects, which would cause the lengths of the ring bonds to vary smoothly with distance from the perturbed center, but follows naturally from a consideration of the effect of a perturbation of the Coulomb parameters of the substituted phosphorus atom on the orders of successive bonds. In Figure 8 is shown a comparison of the deviations from the mean P-N bond length in $N_4P_4F_6Me_2$ with the bond order changes calculated by approximate perturbation theory[17] from the formula

$$\pi_{rs,t} = \frac{\partial p_{rs}}{\partial \alpha_t} = 2\Sigma_{j(occ)}\Sigma_{k(unocc)}\frac{c_{jt}c_{kt}(c_{jr}c_{ks} + c_{js}c_{kr})}{E_j - E_k}$$

in which rs and t denote the bonded and perturbed atoms. The qualitative variation of bond lengths shows that the effect of the perturbation is transmitted through four bonds and in itself is good evidence for delocalization; its detailed form, paralleled by the calculated bond atom polarizabilities, shows that the bond length changes are well described in terms of the π-inductive effect of the methyl substituents. The geminal-antipodal $N_4P_4F_4Me_4$ also has its longer P-N bonds meeting in the PMe_2 groups, but since the molecule is symmetrically substituted at both ends, its structure cannot provide evidence of extended transmission of electronic effects. The decreasing mean angle at nitrogen in the series $N_4P_4F_8$ (147°), $N_4P_4F_6Me_2$ (145°), $N_4P_4F_4Me_4$ (135°), and $N_4P_4Me_8$ (132°) does, however, show that as the mean ligand electronegativity is decreased, electrons are progressively localized on nitrogen.

The reactivity of phosphonitrilic derivatives to nucleophiles can also be interpreted in terms of π-electron density. The energetically higher component of the dual π system is homomorphic,[18] as shown by the oscillation of the first ionization potentials of the phosphonitrilic fluorides,[7] and both the π-electron density at phosphorus calculated on this basis and the measured activation energy for a bimolecular substitution reaction of the phosphonitrilic chlorides alternate with ring size in the same way (Table II).

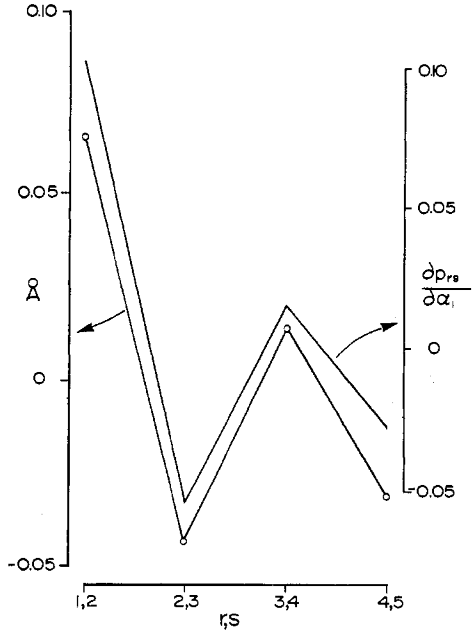

Figure 8. Deviations of lengths of successive PN bonds in *gem*-$N_4P_4Me_2F_6$ from mean length (left-hand scale) and atom bond polarizabilities (right-hand scale, unit β^{-1}, $\alpha_N = \alpha_P + \beta$). Abscissa denotes bond; atoms numbered as in Figure 7.

Table II. π-Electron Densities[a] and Activation Energies[b]

	n			
	3	4	5	6
π density on P	0.621	0.523	0.582	0.551
E_{act}, kcal mol^{-1}	18.3	16.3	17.0	16.3

[a] HMO calculations for homomorphic π systems in $(NP)_n$; $\alpha_N = \alpha_P + \beta$. [b] For reaction of $(NPCl_2)_n$ with Cl^- (D. B. Sowerby, *J. Chem. Soc.*, 1396 (1965)).

As a first approximation, we consider reactivity in terms of π-electron density and its perturbation by a substituent which alters only the Coulomb parameter of the substituted atom. Table III gives values of the mutual atom polarizability

$$\pi_{r,t} = \frac{\partial q_r}{\partial \alpha_t} = 4\Sigma_{j(occ)}\Sigma_{k(unocc)}\frac{c_{jt}c_{kt}c_{jr}c_{kr}}{E_j - E_k}$$

calculated for t = 1 for an N_4P_4 ring, for two relative electronegativities of nitrogen and phosphorus. In both cases, the methyl-substituted phosphorus atom acquires a partial positive charge, π-electron density being distributed elsewhere in the ring in a way which depends on the relative orbital electronegativities of phosphorus and nitrogen. The π-inductive effect is therefore expected to result in *gem*-dimethylation; in practice, it would be partly offset by the opposing σ-inductive effect, which reduces the difference between different positions in the same molecule. A further result is that as ρ increases, charge polarization decreases, and, with it, specific orientational effects of the substituent. For the eight-membered ring, no phosphorus atom bearing a partial positive charge remains for the third methyl group, which (on the simple basis adopted here) therefore enters, by default, when the negative charge is least. For $\rho = 1$, there is no preference; for $\rho = 2$, antipodal substitution is to be expected for the third and fourth substituents, as found.

The successful interpretation of the orientation pattern in terms of a π-inductive effect can be extended to the six-membered and ten-membered rings, in which the more pronounced preference for geminal dimethylation is accompanied

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Table III. Mutual Atom Polarizabilities,[a] $\pi_{r,1} = \partial q_r/\partial \alpha_1$

	Atom (r)				
	1	2	3	4	5
$\rho = 1$	+0.273	−0.096	−0.023	−0.006	−0.023
$\rho = 2$	+0.166	−0.068	−0.010	−0.003	−0.004

[a] HMO calculations; $\alpha_N = \alpha_P + \rho\beta$; homomorphic.

by an addition reaction, which can be understood similarly, and a preliminary account of this work has appeared.[19] Conjugative,[20] solvent, and reagent effects are also important and will be considered later.

Registry No. MeLi, 917-54-4; $N_4P_4F_8$, 14700-00-6; $MeN_4P_4F_7$, 37110-97-7; 1,1-$Me_2N_4P_4F_6$, 29021-59-8; *trans*-1,5-$Me_2N_4P_4F_6$, 37110-98-8; $Me_2N_4P_4F_6$, 37164-25-3; 1,1,3-$Me_3N_4P_4F_5$, 37110-93-3; 1,1,5-$Me_3N_4P_4F_5$, 37110-94-4; 1,1,5,5-$Me_4N_4P_4F_4$, 29144-50-1; $Me_8N_4P_4$, 4299-49-4.

Acknowledgments. We thank the National Research Council of Canada for financial support, the University of British Columbia for a University Graduate Fellowship (to T. N. R.), and Dr. L. D. Hall and Mr. R. Burton for the heteronuclear decoupling experiments.

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Contribution from the Department of Chemistry,
Georgetown University, Washington, D. C. 20007

Hydroxide Ion as a Reducing Agent for Cations Containing Three Ruthenium Atoms in Nonintegral Oxidation States

JOSEPH E. EARLEY* and TERENCE FEALEY

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Hydroxide ion is oxidized by $Ru(NH_3)_5ORu(NH_3)_4ORu(NH_3)_5^{7+}$ in a second-order reaction for which k is 1.9×10^4 sec^{-1} M^{-1} (at 25° in buffered media of ionic strength 0.25 M) and $\Delta H^{\ddagger}$ is 19 kcal/mol. An isosbestic point exists throughout the reaction but chemical evidence shows than an intermediate is involved. The corresponding oxidant which has two ethylenediamine ligands replacing the four ammonias on the central ruthenium atom is reduced faster but with a similar $\Delta H^{\ddagger}$. The spectra of the four ruthenium trimers involved in these reactions are consistent with a molecular orbital scheme. All the data are consistent with a mechanism involving rate-determining attack of OH^- on the central ruthenium atom.

There have been reports[1,2] of a curious reaction by which OH^- is rapidly oxidized by $(NH_3)_5RuORu(NH_3)_4ORu(NH_3)_5^{7+}$ ("ruthenium brown," hereafter I) with the production of the corresponding 6+ cation ("ruthenium red," hereafter II). Previous workers[1] suggested that the OH radical was the oxidation product of OH^-, but this seems unlikely since the I → II potential is only 0.75 V *vs.* the normal hydrogen electrode, which appears insufficient[3] to produce OH. Strong oxidants such as MnO_4^- normally react with OH^- only quite slowly,[4] but the ruthenium trimer I reacts rapidly with OH^-. We have investigated this system to determine why such a mild oxidant oxidizes OH^- so readily.

We recently described[5] the synthesis of an analog of the 6+ ion with two ethylenediamine (en) groups replacing the NH_3 groups on the central ruthenium atom and also an X-ray structure determination of this ion. We now report spectra of four interrelated compounds (en and NH_3, 6+ and 7+). The remarkable reactivity of I with OH^- can be rationalized on the basis of a molecular orbital scheme based on these spectra.

Experimental Section

$LiClO_4$ was prepared from Li_2CO_3 and $HClO_4$, digested in solution overnight at 40–50° to remove SiO_2, and recrystallized three times from triply distilled water.

The chloride salt of "ruthenium red" (II) was prepared as follows. $RuCl_3 \cdot 3H_2O$ (5 g) was dissolved in 25 ml of 0.25 M HCl. Absolute alcohol (5 ml) and ascorbic acid (0.1 g) were added and the brown solution was refluxed at 85° for 3 hr and then concentrated to 5 ml under reduced pressure. Concentrated NH_3 (20 ml) was added a few milliliters at a time and the mixture was held at 85–90° for 1 hr while streams of air and ammonia gas were passed through the solution. Concentrated ammonia solution was added as necessary to maintain the volume of the reacting solution at approximately 20 ml. The reaction mixture was centrifuged while hot, and the supernatant liquid was then cooled in an ice bath. A brown powder was collected by filtration, recrystallized from 0.1 M ammonia, and washed with ethanol and ether (yield 2 g). *Anal.* Calcd for $Ru_3O_2(NH_3)_{14}Cl_6 \cdot 3H_2O$: Ru, 36.10; N, 23.33; Cl, 25.31. Found:[6] Ru, 36.12; N, 23.10; Cl, 27.58.

In order to prepare the chloride salt of ruthenium brown (I), the chloride of II (1.0 g) was dissolved in water at 40° and 2 M HCl was added until the pH of a cooled aliquot was 1.0. A stream of air was then passed through the warm solution for several hours. The mixture was cooled and a brown powder was collected by filtration and washed with 0.1 M HCl and ether (yield 0.8 g). *Anal.* Calcd for $Ru_3O_2(NH_3)_{14}Cl_7 \cdot 2H_2O \cdot HCl$: Ru, 33.82; N, 21.90; Cl, 31.69. Found: Ru, 33.48; N, 21.90; Cl, 31.18. Needle-shaped crystals were grown by rapid evaporation of solutions of the chloride of I.

The ethylenediamine (en) analog of II, namely, $Ru_3O_2(NH_3)_{10}(en)_2Cl_6 \cdot H_2O$ (hereafter II′), was prepared as previously described.[5] In order to prepare the oxidized analog (hereafter I′), 50 mg of II′ chloride was dissolved in a minimum quantity of water. The solution was acidified and 2 drops of chlorine water (~10 mM) were added. The color of the solution rapidly changed from red to brown. A few drops of a saturated solution of NaCl in 0.01 M HCl

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