Nuclear Magnetic Resonance Investigations of Boron Compounds. Part 15.[1] Some Derivatives of a Triazaphosphadiborine and a Triazaphosphaborolidine

By **Kleomenis Barlos, Heinrich Nöth, and Bernd Wrackmeyer,*** Institut für Anorganische Chemie der Universität München, Meiserstr. 1, D-8000 München 2, Germany
William McFarlane, Sir John Cass School of Science and Technology, City of London Polytechnic, 31 Jewry Street, London EC3N 2EY

N.m.r. parameters (^{1}H, ^{11}B, ^{13}C, and ^{31}P) of a triazaphosphadiborine and a triazaphosphaborolidine and their corresponding ' phosphinylium ' cations have been measured. The geminal ^{31}P–^{13}C coupling constants are consistent with non-planarity of the ring systems, this non-planarity being greater in the neutral than in the cationic species. Values of $^3J(^{31}$PNCH) are less sensitive to changes in ring conformation and therefore must be used with care to assess this unless independent evidence is available.

THE chemistry of compounds with P–N bonds has been stimulated by the discovery of cyclic systems containing two-co-ordinate phosphorus(III);[2-5] the λ^3-PN heterocycles, in particular, form readily and are of special interest in connection with the nature of the P–N bond and the extent of electron delocalization.[6-8] However, so far no satisfactory conclusions regarding d_π–p_π P–N bonding have emerged in spite of numerous determinations of P–N bond lengths by *X*-ray and electron-diffraction techniques,[9] ionization-potential measurements, and molecular-orbital calculations.[10]

Hydrogen-1 and ^{13}C n.m.r. studies of acyclic aminophosphines have revealed significant barriers to rotation about the P–N bond, and this has been interpreted both in terms of d_π–p_π bonding,[11] and of repulsion between the lone electron pairs on the phosphorus and nitrogen atoms.[12] This latter interpretation is analogous to that found in hydrazines[13] and it has been pointed out recently[14] that pyramidal inversion at nitrogen should also be taken into account in discussing the torsional motion. For acyclic aminophosphines valuable information on the internal rotation about the P–N bond is provided by the couplings $^3J(^{31}$PNCH),[12,15] $^2J(^{31}$PN-^{13}C),[16] and $^2J(^{31}$PN^{31}P),[17,18] and thus it appears likely that these parameters could be used to deduce the conformation adopted by cyclic species.[10,20] We have therefore examined four closely related heterocycles containing nitrogen, phosphorus, and boron, and report here ^{1}H, ^{11}B, ^{13}C, and ^{31}P n.m.r. data which enable us to draw conclusions about the degree of planarity of the ring systems.

EXPERIMENTAL

2-*Chloro*-1,3,4,5,6-*pentamethyl*-1,3,5,2,4,6-*triazaphosphadiborine*, (2).—Heptamethyl-1,3,5,2,4,6-triazasiladiborine[21] (9.8 g) was condensed with liquid N$_2$ and PCl$_3$ (6.8 g) was added. After warming to room temperature, stirring of the liquid was continued for 1 h, and the mixture brought to reflux for 60 min. Dichlorodimethylsilane which formed was removed *in vacuo*. On distillation of the residue the *product* (7.7 g, 75%) was obtained as a greenish liquid, b.p. 47 °C (1 Torr),† which became yellow on heating [Found: C, 28.5; H, 7.4; B, 10.2; Cl, 16.4; N, 19.5%; *M* = 205 (^{11}B, ^{35}Cl mass spectra). $C_5H_{15}B_2ClN_3P$ requires C, 29.3; H, 7.4; B, 10.5; Cl, 17.3; N, 20.5%; *M* = 205.2].

1,3,4,5,6-*Pentamethyl*-1,3,5,2,4,6-*triazaphosphadiborin*-2-*ylium Tetrachloroaluminate*(III), (3).—A slurry of AlCl$_3$ (1.95 g) in pentane (20 cm^3) was cooled to −78 °C. With stirring, the phosphaborazine (2) (3.0 g) dissolved in pentane (5 cm^3) was added. A nearly clear solution resulted on slowly warming to room temperature. Crystals settling from the mixture were collected after 3 h and washed five times with portions (3 cm^3) of pentane to give the *product* (4.6 g, 93%), decomp. 120 °C (Found: C, 17.7; H, 3.9; N, 11.5. $C_5H_{15}AlB_2Cl_4N_3P$ requires C, 17.7; H, 4.5; N, 12.4%). Attempted recrystallization from CH$_2$Cl$_2$,C$_6$H$_6$, tetrahydrofuran–pentane, or OEt$_2$–CH$_2$Cl$_2$ gave an oil.

3-*Chloro*-1,2,4,5-*tetramethyl*-1,2,4,3,5-*triazaphosphaborolidine*, (4).—Heptamethyl-1,2,4,3,5-triazasilaborolidine (38 mmol) in anhydrous CH$_2$Cl$_2$ (25 cm^3) was treated with PCl$_3$ (38 mmol) in CH$_2$Cl$_2$ (30 cm^3) at −78 °C. The stirred mixture was warmed slowly to room temperature and the reaction was found (^{1}H n.m.r.) to be complete after 2 h. Solvent and SiMe$_2$Cl$_2$ were removed *in vacuo* to leave the *product* (4.9 g, 72%) as a viscous liquid, b.p. 52 °C (2 Torr), which solidified on standing (Found: C, 26.6; H, 6.6; B, 6.2; Cl, 19.70; N, 22.9. $C_4H_{12}BClN_3P$ requires C, 26.8; H, 6.7; B, 6.0; Cl, 19.8; N, 23.4%).

1,2,4,5-*Tetramethyl*-1,2,4,3,5-*triazaphosphaborolidin*-3-*ylium Tetrachloroaluminate*(III), (5).—Aluminium chloride (1.55 g) in CH$_2$Cl$_2$ (10 cm^3) was dropped at 0 °C into a stirred solution of (4) (2.15 g) in CH$_2$Cl$_2$ (3 cm^3). After 2 h the ^{1}H n.m.r. spectrum still showed the presence of unchanged starting material and sufficient AlCl$_3$ was then added to saturate the solution. Removal of small amounts of solid followed by addition of pentane (15 cm^3) gave an oil which contained (^{1}H n.m.r.) only the cationic species, but attempts to crystallize the oil were unsuccessful. Prolonged pumping at 40 °C (1 Torr) gave a waxy material whose ^{1}H, ^{13}C, and ^{31}P n.m.r. parameters were consistent with the proposed formulation as a 1 : 3 *adduct* (Found: C, 7.9; H, 2.4; N, 7.4. $C_4H_{12}Al_3BCl_{10}N_3P$ requires C, 8.3; H, 2.1; N, 7.3%). A solution of the adduct in CHCl$_3$ had high electrical conductivity. Attempts to make other solid derivatives (*e.g.* tetraphenylborate) led to waxes of variable composition, and quantitative conductivity measurements were not pursued in view of the uncertainty of the precise nature of the anion in solution.

Hydrogen-1 n.m.r. spectra were recorded using a Varian A-60 spectrometer; ^{1}H-{X} double-resonance experiments were performed at 23 °C on a JEOL C60-H spectrometer with

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† Throughout this paper: 1 Torr = (101 325/760) Pa.

a modified probe. Power at the X resonance frequency was supplied *via* a tuned amplifier by a Schumberger FS-30 frequency synthesizer which also controlled the basic spectrometer frequency. Boron-11 and ^{31}P n.m.r. spectra were obtained on a Varian HA-100 spectrometer, ^{13}C n.m.r. data on Varian FT-80 [compound (1)], JEOL FX-60 [(2), (4), and (5)], JEOL FX-100 [(2)], and Bruker WP-200 spectrometers.

RESULTS AND DISCUSSION

The species studied and their n.m.r. parameters are in the Table. 2-Chloro-1,3-dimethyl-1,3,2-diazaphospholidine (1), whose structure is known,[22] and the bis(dimethylamino)phosphinylium cation (6) [23] are included for comparison, and assignments and signs of coupling constants [relative [24] to $^1J(^{13}CH) > 0$] are based on the results of $^1H-\{^{13}C\}$, $^1H-\{^{31}P\}$, and $^{13}C-\{^1H\}$ double-resonance experiments. The geminal coupling $^2J(^{31}PN^{13}C)$ is temperature-independent [20] in amino-derivatives of (1) and it is reasonable to assume that this is also true of compounds (1)—(5).

N.m.r. parameters [a] for cyclic phosphorus–nitrogen compounds

	δ(^{1}H)			δ(^{11}B)	δ(^{13}C)			δ(^{31}P)	$J(^{31}P,H)$			$J(^{31}P,^{13}C)$		
Compound	CH$_3$	CH'$_3$	CH''$_3$		CH$_3$	CH'$_3$	CH''$_3$		CH$_3$	CH'$_3$	CH''$_3$	CH$_3$	CH'$_3$	CH''$_3$
(1) ClPN(CH$_3$)CH$_2$CH'$_2$N(CH$_3$) [b]	2.58	3.12	3.26		33.2	52.9		172.5	+15.6	+3.5	+10.9	+18.6	−10.8	
(2) ClPN(CH$_3$)B(CH'$_3$)N(CH''$_3$)B(CH'$_3$)N(CH$_3$) [c]	3.01	0.53	2.91	37.0	32.6	0.1	33.3	160.2	+17.5	?	±1.0	+42.7	?	±22
(3) +PN(CH$_3$)B(CH$_3$)N(CH''$_3$)B(CH'$_3$)N(CH$_3$) [d]	3.55	0.8	3.16	38.6	38.1	0.6	32.5	302.0	+15.5	?	±1.0	+34.4	?	±4.9
(4) ClPN(CH''$_3$)B(CH'''$_3$)N(CH'$_3$)N(CH$_3$) [e]	3.07	3.06	2.99	32.6	32.0	31.8	29.3	166.0	+17.5	±1.8	+15.0	+12.1	?	+21·1
(5) +PN(CH''$_3$)B(CH$_3$)N(CH'$_3$)N(CH$_3$) [f]	3.51	3.15	3.10	34.0	34.6	33.0	31.3	228.0	+12.5	±2.8	+12.0	+16.6	±3.9	+21.0
(6) +P[N(CH$_3$)$_2$]$_2$ [g]	1.97	2.13			52.4	54.6			±4.8	+14.1		±6.3	+19.5	

[a] Coupling constants are in Hz, ±0.2 Hz. Chemical shifts are in p.p.m. to high frequency (low field) of the reference compound: ^{1}H, SiMe$_4$, ±0.01 p.p.m.; ^{11}B, external OEt$_2$·BF$_3$, ±0.1 p.p.m.; ^{13}C, SiMe$_4$, ±0.1 p.p.m.; ^{31}P, external 85% H$_3$PO$_4$, ±0.1 p.p.m. [b] Proton data from ref. 19; CH'$_3$ CH''$_3$ refer to the inequivalent CH$_2$ groups in this compound. $^1J(^{31}P,^{15}N)$ +63.3 Hz. [c] In C$_6$D$_6$ (*ca.* 30%). [d] In CD$_2$Cl$_2$ (*ca.* 30%). [e] In C$_6$D$_6$, δ(^{1}H) (B–CH$_3$) 0.41, δ(^{13}C)(B–CH$_3$) −5.7 p.p.m. [f] CDCl$_3$ (*ca.* 30%). [g] From ref. 22.

The conformations of (4) and (5) should be quite similar to that of (1), but there will be marked differences between these and the six-membered rings (2) and (3). Although it would normally be expected that the sp^2-hybridized nitrogen and boron atoms will favour planar ring structures in order to achieve maximal boron–nitrogen p_π–p_π overlap, as exemplified by the borazines,[25] it is also possible for twisted structures to arise, as for example in the hexahydrotetra-azadiborines.[26] This kind of interaction will tend to keep any N–B–N unit planar, and will therefore confer greater rigidity upon (2) than (4), while the tendency of the nitrogen lone pairs of the hydrazine unit in (4) to adopt a *gauche* conformation will make (4) more rigid than (1).

It has been shown that the magnitudes and signs of the coupling constants $^2J(^{31}PX)$ and $^3J(^{31}PX)$ depend mainly on the orientation of the phosphorus lone pair.[15,16] In our case the relevant couplings are $^2J(^{31}PN^{13}C)$ and $^3J(^{31}PNCH)$ and it is known that these both have large positive values when the dihedral angle ϕ between the N–C or the C–H bond and the phosphorus lone-pair direction is small. As ϕ approaches 180° these two couplings become small and may even become negative. In species (1)—(5) all the relevant couplings are positive and of fairly large magnitude, indicating rather small values of ϕ.

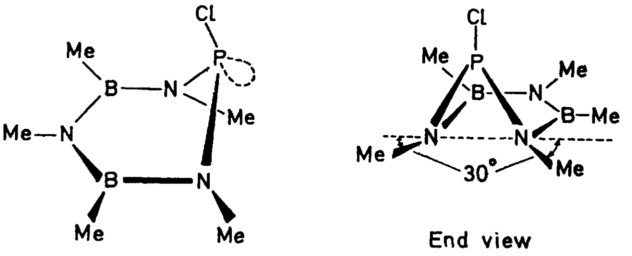
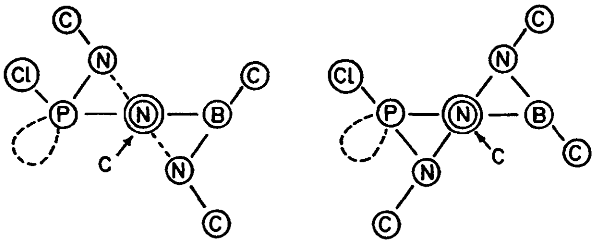


FIGURE 1 Proposed structure of (2)

For (2) the coupling $^2J(^{31}PN^{13}C)$ is considerably larger than for (1), suggesting that the corresponding lone-pair dihedral angle is smaller in the former molecule. Other five- and six-membered rings containing a P–Cl unit have P–N–Cl interbond angles of 100—105°,[9,22,27,28] and on this basis only a non-planar ring can account for the size of $^2J(^{31}PN^{13}C)$ in (2). Figure 1 shows a suggested conformation for (2) in which the phosphorus atom lies out of the plane of the NBNBN fragment, and in which the *N*-methyl groups adjacent to phosphorus are also out of this plane. Examination of a model shows that if the associated C–N bonds make an angle of *ca.* 30° with the NBNBN plane then the lone pair–C–N dihedral angle will be *ca.* 15°, which is consistent with the observed size of $^2J(^{31}PN^{13}C)$. An advantage of the proposed planar NBNBN arrangement is that it permits the nitrogen and boron atoms to be sp^2 hybridized so as to achieve maximum p_π–p_π overlap, and it is noteworthy that the boron chemical shift of (2) is quite similar to those of planar hexamethylborazine [mean δ(^{11}B) 35 p.p.m.] [29] and chloropentamethylborazine [δ(^{11}B) 36.3 p.p.m.].[29] This last result further indicates that replacement of BCl by PCl has little effect on the effective electronic charge of the remote boron atom.

In the five-membered ring system (4) markedly different values of $^2J(^{31}PN^{13}C)$ are found for the two *N*-methyl groups adjacent to phosphorus and this suggests that the molecule adopts a twisted conformation leading to different dihedral angles between the phosphorus lone-pair direction and the two C–N bonds. This interpretation is confirmed by the fact that for (1) the coupling constant differs for the CH$_3$ and the CH$_2$ groups in a manner consistent with the expected smaller dihedral angle for the former. In fact, it appears that in (4), ϕ is larger for the CH$_3$N(N) than the CH$_3$N(B) group, and this can be understood in terms of a *gauche* conformation of the hydrazine fragment. Moreover, the nitrogen atom bound to phosphorus in this fragment may not be sp^2 hybridized,[30] whereas the corresponding nitrogen atom in the PNB fragment probably is. This kind of situation is known to occur in pentamethyl-1,2,4,3,5-triazadiborolidine [31] and in 3,5-dichloro-1,2,4-trimethyl-1,2,4,3,5-triazadiphospholidine.[32] It is certainly clear that the ring of (4) cannot be planar, and taking into account the value of $\delta(^{11}B)$ which is within the range observed for compounds having CBN_2 units,[29] two conformations can be suggested as shown in Figure 2. Each of these permits good boron–nitrogen p_π–p_π overlap and a *gauche* conformation of the hydrazine fragment. However, only 2(*a*) is in accord with the values observed for $^2J(^{31}PN^{13}C)$, since in 2(*b*) the rather small lone pair–C–N(N) dihedral angle is inconsistent with the comparatively small size of the coupling constant, and we therefore conclude that this [2(*a*)] is the conformation adopted. It is of interest to note that the values of $^3J(^{31}PNCH_3)$ would not permit one to make a similar discrimination, since they are rather similar for (1), (2), and (4), this being a consequence of rather close similarities of the relevant dihedral angles in these three molecules. Thus in this type of system the coupling $^2J(^{31}PN^{13}C)$ is much more sensitive than $^3J(^{31}PH)$ to conformational changes and is correspondingly more valuable as a structural diagnostic.



(*a*) (*b*)

FIGURE 2 Proposed conformations of (4)

The change from the neutral ring systems (2) and (4) to the corresponding ' phosphinylium ' cations (3) and (5) is accompanied by a large deshielding at phosphorus but by only a small deshielding at boron. This suggests that the overall change in electron density at boron is small, although there is some loss of π-charge density at boron.[33] The large change in $\delta(^{31}P)$ indicates that cationic P^{III} is able to compete more effectively than neutral P^{III} for the electron density of the adjacent nitrogen atoms, but without nitrogen n.m.r. data it is not possible to say whether this involves a π- or σ-bonding mechanism. Only a single resonance signal was found in the proton-decoupled ^{31}P spectra of our samples, and it appears that substantial deshielding of phosphorus, accompanied by high frequency shifts of the proton and ^{13}C signals, is characteristic of the formation of a ' phosphinylium ' cation.

From low-temperature ^1H and ^{13}C n.m.r. studies [23,34] of the bis(dimethylamino)phosphinylium cation (6) it is known that $^2J(^{31}PN^{13}C)$ and $^3J(^{31}PNCH)$ depend on the phosphorus electron lone-pair orientation as in the neutral molecules. The smaller value of $^2J(^{31}PN^{13}C)$ of (3) as compared with (2) is therefore consistent with a flatter ring structure and a shift towards sp^2 hybridization of cationic P^{III} in (3), since each of these would increase the lone pair–C–N dihedral angle. These changes would increase the ability of phosphorus to participate in the delocalized π-bonding system and the observation that $^4J(^{31}PNBN^{13}C) = 4.9$ Hz for (3) as compared with <2 Hz for (2) may reflect this.

A similar comparison of (4) and (5) shows that while $^2J(^{31}PN^{13}C)$ hardly changes for the PNB fragment, there is a marked difference for the PNN fragment which suggests that ϕ is reduced in this part of (5). This is again consistent with a closer approach to planarity in the cation which would be compatible with stronger π bonding leading to a reduced tendency for the hydrazine fragment to adopt a *gauche* conformation. By contrast, the constancy of the lone pair–C–N(B) dihedral angle suggests that there is little difference in phosphorus hybridization between (4) and (5), although this conclusion may be affected somewhat by unknown variations in bond lengths and interbond angles between the two species. Nevertheless, it does appear that it is the hydrazine moiety which experiences the greatest structural change in passing from (4) to (5), and this conclusion is reinforced by the greater change in $\delta(^1H)$ observed for the $CH_3N(N)$ (0.44 p.p.m.) compared with the $CH_3N(B)$ (0.11 p.p.m.) protons.

In principle $^3J(^{31}PNB^{13}C)$ should also give conformational information on these systems, but in practice the $^{13}C(B)$ resonances are seriously broadened by partially relaxed scalar coupling to the quadrupolar boron nuclei, and it was not possible to measure this coupling constant. Similar remarks apply to $^4J(^{31}PNBCH_3)$, although in this case irradiation at the ^{31}P resonance frequency gave some sharpening of the proton resonance, thus indicating that the coupling is not zero.

Our main conclusions are that the heterocyclic rings (2) and (4) are non-planar, although p_π–p_π interactions lead to planar NBN fragments. In (3) and (5) a degree of participation by phosphorus in the π system leads to flatter rings, and in all cases the geminal ^{31}P–^{13}C coupling constants are more valuable than the vicinal ^{31}P–^1H was in providing conformational details. This, however, is largely due to the geometrical peculiarities of these systems. It is hoped that direct structural studies by diffraction methods will eventually support these conclusions, but it has not yet been possible to obtain suitable single crystals of any of the four new compounds reported in this paper. Efforts in this direction are continuing and meanwhile it is clear that ^{13}C n.m.r. measurements, particularly when series of closely related compounds are available, are a valuable alternative source of information.

We thank the Deutsche Forschungsgemeinschaft and the S.R.C. for support.

[8/606 *Received, 3rd April,* 1978]

REFERENCES

[1] Part 14, H. Fusstetter, H. Nöth, B. Wrackmeyer, and W. McFarlane, *Chem. Ber.*, 1977, **110**, 3172.

[2] Y. Charbonnel and J. Barrans, *Tetrahedron*, 1976, **32**, 2039.

[3] E. Niecke and R. Kröher, *Angew. Chem.*, 1976, **88**, 758; *Angew. Chem. Internat. Edn.*, 1976, **15**, 692.

[4] O. J. Scherer and G. Schnabl, *Chem. Ber.*, 1976, **109**, 2996.

[5] S. Fleming, M. K. Lupton, and K. Jehot, *Inorg. Chem.*, 1972, **11**, 2534.

[6] H. Nöth and R. Ullmann, *Chem. Ber.*, 1976, **109**, 942.

[7] M. K. Das and J. J. Zuckermann, *Inorg. Chem.*, 1971, **10**, 1028.

[8] W. Zeiss, W. Schwarz, and H. Hess, *Angew. Chem.*, 1977, **89**, 423.

[9] D. E. C. Corbridge, 'The Structural Chemistry of Phosphorus,' Elsevier, New York, 1974; J. C. Clardy, R. L. Kolpa, and J. G. Verkade, *Phosphorus*, 1974, **4**, 133.

[10] M. Barthelat, R. Mathis, and F. Mathis, *J.C.S. Chem. Comm.*, 1977, 615; M. Barthelat, R. Mathis, J. F. Labarre, and L. Mathis, *Compt. rend.*, 1975, **C280**, 645; I. G. Csizmachia, A. H. Cowley, M. W. Taylor, L. M. Tel, and S. Wolfe, *J.C.S. Chem. Comm.*, 1972, 1147; I. G. Csizmachia, A. H. Cowley, M. W. Taylor, and S. Wolfe, *ibid.*, 1974, 432; M. H. Whangbo and S. Wolfe, *Canad. J. Chem.*, 1976, **54**, 949; J. G. Hargas and S. D. Worley, *Inorg. Chem.*, 1977, **16**, 186.

[11] D. Imbery and H. Friebolin, *Z. Naturforsch*,. 1968, **B23**, 759; H. Goldwhite and D. G. Mowsell, *Chem. Comm.*, 1969, 713.

[12] A. H. Cowley, M. J. S. Dewar, and W. R. Jackson, *J. Amer. Chem. Soc.*, 1968, **90**, 4185; A. H. Cowley, M. J. S. Dewar, W. R. Jackson, and W. B. Jennings, *ibid.*, 1970, **92**, 5206.

[13] S. F. Nelson, W. C. Hollised, and J. C. Calabrese, *J. Amer. Chem. Soc.*, 1977, **99**, 4461; S. F. Nelson, *Accounts Chem. Res.*, 1978, **11**, 14.

[14] A. H. Cowley, M. W. Taylor, M. H. Whangbo, and S. Wolfe, *J.C.S. Chem. Comm.*, 1976, 838.

[15] A. H. Cowley, M. J. S. Dewar, W. R. Jackson, and W. B. Jennings, *J. Amer. Chem. Soc.*, 1970, **92**, 1085.

[16] M. P. Simonnin, R. M. Lequau, and F. W. Wehrli, *J.C.S. Chem. Comm.*, 1972, 1204.

[17] R. J. Cross, T. H. Green, and R. Keat, *J.C.S. Dalton*, 1976, 1424.

[18] I. J. Colquhoun and W. McFarlane, *J.C.S. Dalton*, 1977, 1674.

[19] J. P. Allbrand, A. Cogue, D. Gagnaire, and J. B. Robert, *Tetrahedron*, 1972, **28**, 819.

[20] J. H. Hargis, S. D. Worley, W. B. Jennings, and M. S. Tolley, *J. Amer. Chem. Soc.*, 1977, **89**, 8090.

[21] K. Barlos, Dissertation, University of Munich, 1977.

[22] V. A. Naumov, N. A. Gulyeva, and M. A. Pudovik, *Doklady Akad. Nauk. S.S.S.R.*, 1972, **203**, 590.

[23] M. G. Thomas, R. W. Kopp, C. W. Schultz, and R. W. Parry, *J. Amer. Chem. Soc.*, 1974, **96**, 2646.

[24] W. McFarlane, *Quart. Rev.*, 1969, **23**, 187.

[25] J. J. Lagowski, *cf.* Gmelin, 'Handbuch der Anorganischen Chemie,' Ergänzungswerk zur 8. Auflage, 1975, **22**, 321.

[26] J. C. Huffman, H. Fusstetter, and H. Nöth, *Z. Naturforsch.*, 1976, **B31**, 289.

[27] H. Nöth and R. Ullmann, *Chem. Ber.*, 1976, **109**, 1089.

[28] N. M. Zaripov, V. A. Naumov, and L. L. Tuzova, *Phosphorus*, 1974, **4**, 145; V. A. Naumov, V. M. Bezzulov, and M. A. Pudovik, *J. Strukt. Khim.*, 1975, **16**, 3.

[29] H. Nöth, and B. Wrackmeyer, '^{11}B-NMR-Spectroscopy, NMR Basic Principles and Progress,' vol. 14, eds. P. Diehl, E. Fluck, and R. Kosfeld, Springer Verlag, Heidelberg, New York, 1978.

[30] W. van Doorne, G. W. Hunt, R. W. Parry, and A. W. Cordes, *Inorg. Chem.*, 1971, **10**, 2951.

[31] H. Fusstetter, Dissertation, University of Munich, 1977.

[32] H. Nöth and R. Ullmann, *Chem. Ber.*, 1976, **109**, 2581.

[33] J. Kroner, D. Nölle, and H. Nöth, *Z. Naturforsch.*, 1973, **B28**, 413.

[34] M. G. Thomas, C. W. Schultz, and R. W. Parry, *Inorg. Chem.*, 1977, **16**, 994.