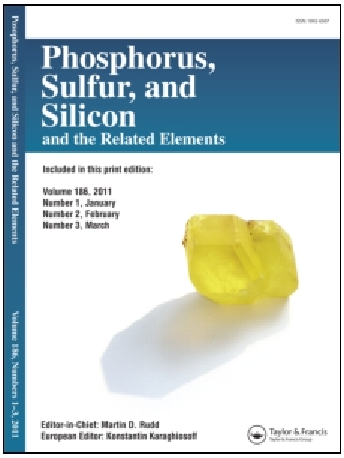

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SOME EFFECTS OF ORBITAL CONSTRAINT IN TRIS(DIALKYLAMINO)PHOSPHINES

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SOME EFFECTS OF ORBITAL CONSTRAINT IN TRIS(DIALKYLAMINO)PHOSPHINES

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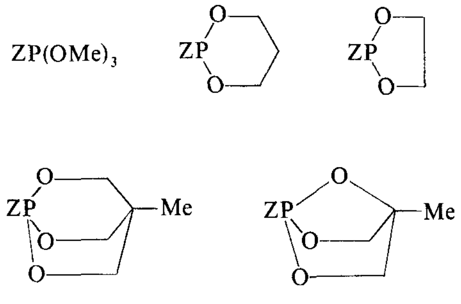
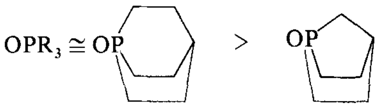
The syntheses of the new cages $P(NMeNMe)_3PO$, $H_3BP(NMeNMe)_3PO$, $H_3BP(NMeNMe)_3PNPh$ and $OP(NMeNMe)_3PNPh$ are reported. From the ir spectra of acyclic and bicyclic aminophosphine BH_3 adducts and oxides in the BH and O=P stretching regions, respectively, it has been determined that the stretching frequencies of these groups increase upon molecular constraint. Moreover, νBH appears to be sensitive to the pi bonding nature of the phosphorus substituent at the other end of the cage in $H_3BP(NMeNMe)_3PZ$ systems. Separate linear correlations of δCH_2 and $^3J^{31}P^1H$ are observed in a series of $YP(NMeCH_2)_3CMe$ compounds where the sigma accepting and sigma accepting plus pi donating Y group ranges in electronegativity. Dipole moment studies show that constraint of $YP(NMe_2)_3$ into bicyclic $YP(NMeCH_2)_3CMe$ analogs results in little change in molecular moment in contrast to moments for $YP(OMe)_3$ when compared to those of $YP(OCH_2)_3CMe$ systems.

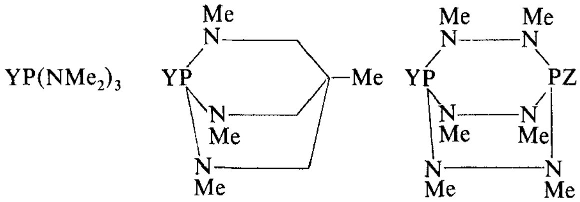
Dramatic changes in the Lewis basicity[1–3] and metal-ligating properties[4,5] accompany the constraint of acyclic phosphite esters into monocyclic ring systems and cages. Thus while the Lewis basicity of the phosphorus (Z = lone pair) or phosphoryl oxygen (Z = O) in the series below decreases from left to right, the pi acceptor properties of phosphorus (Z = lone pair) appear to augment. These trends have been ascribed to



preferential rehybridization of the esteratic oxygens (hinge effect) compared to that which occurs in the relatively rigid OPO angles, and to the spatial reorientation of esteratic oxygen lone pair orbitals relative to the phosphorus lone pair or to the phosphoryl O=P bond. Additional support for these ideas has recently come from spectroscopic studies of the hydrogen bonding tendencies of the phosphoryl oxygen in several phosphine oxides which follow the order:[6]



The absence of esteratic oxygens here permits no appreciable change in the phosphoryl oxygen basicity within the first two members of the series. Strain in the CPC angles of the last member, however, introduces more s character into the O=P bond, thereby reducing the basicity of the



Y	Y	Y	Z
(**1**) lone pair	(**2**) lone pair	(**3**) lone pair	O
(**5**) H_3B	(**6**) H_3B	(**4**) lone pair	NPh
(**10**) O	(**11**) O	(**7**) H_3B	O
		(**8**) H_3B	NPh
		(**9**) H_3B	BH_3
		(**12**) O	O
		(**13**) O	NPh

phosphoryl oxygen. Evidence for an increase in positive charge on phosphorus upon constraint has also come from ^{1}JPH values of the protonated phosphite esters,[2] pes[7,8] and icr studies[8] of these esters, and CNDO/2 calculations on the phosphate derivatives.[2]

Here we report ir and nmr spectroscopic observations and dipole moment measurements which provide information regarding phosphorus lone pair donation changes on constraint of acyclic (**1**) into the bicyclic compounds (**2**)–(**4**). The donation properties of phosphorus in these amino phosphines are examined in the BH_3 adducts (**5**)–(**9**), and the phosphoryl compounds (**10**)–(**13**).

EXPERIMENTAL

Infrared spectra were recorded on a Beckman IR 4250 spectrophotometer using a polystyrene standard as a reference. Mass spectra were obtained on an AEI MS902 high resolution instrument. Exact masses were obtained by peak matching. Dipole moments were measured on an instrument described elsewhere.[9a] The solutions used were in the range of 10^{-3} to 10^{-2} mole fraction in toluene and were always manipulated under a nitrogen atmosphere. ^{1}H nmr spectra were recorded on a Varian HA-100 spectrometer using TMS as an internal standard.

Compounds (**1**) and (**10**) were purchased from Aldrich Chemical Company and (**1**) was distilled before use. Compounds (**2**),[9b] (**4**),[10] (**5**),[11] (**9**),[12] (**12**),[12] $P(NMeNMe)_3P$,[12] $MeC(CH_2NMe)_3PNPh$[10] and $[MeC(CH_2NMe)_3PCPh_3]BF_4$[9c] were prepared as described elsewhere.

$P(NMeNMe)_3P{=}O$, (**3**) A solution of 2.50 g (10.6 mMol) of $P(NMeNMe)_3P$ in 40 ml of freshly dried acetonitrile was made up under nitrogen at room temperature. This was then cooled in a carbon tetrachloride/dry ice bath which caused considerable precipitation. With vigorous stirring, 543 μl (10.5 mMol) of Br_2 were added dropwise to the solution over a period of 30 minutes. Each drop of bromine produced a bright yellow precipitate which dissolved in the acetonitrile. The mixture was then stirred at −23° for 15 minutes after all the bromine had been added. Quickly adding 191 μl of twice-distilled water to the flask *via* syringe caused the yellow coloration to disappear. Four minutes after adding the water, 2.95 ml (21.2 mMol) of triethylamine was added which caused the precipitation of a copious amount of white solid. The mixture was warmed to room temperature, filtered and the volatiles removed *in vacuo*. The solid residue was then sublimed at 110° (0.01 torr) for 12 hours and this white sublimate (a mixture of the product and some triethylammonium bromide) was resublimed at 70° (0.01 torr) for 6 hours to give 0.80 g (30%) of (**3**) (Mp 210–213°; *M/e* for P^+, 242.1018 ± 0.0013, calcd 252.1018).

$MeC(CH_2NMe)_3PBH_3$, (**6**) While this compound was reported previously[13] by reacting (**2**) and B_2H_6 at low temperatures in ether solution, the present work took advantage of the ready availability of $THFBH_3$ as a convenient source of BH_3.

To a solution of 0.54 ml (3.0 mMol) of (**2**) in 25 ml of ether was added 3.0 ml of a 1.0 *M* $THFBH_3$ solution dropwise at room temperature. The clear colorless solution became turbid and was stirred for 10 hours after which the volatiles were removed and the residue dried *in vacuo*. Sublimation at 80° (0.01 torr) gave 0.52 g (87%) of the white solid (mp 76–77°).

$H_3BP(NMeNMe)_3P{=}O$, (**7**) The mixture, formed by adding 1 ml of 1 *M* $THFBH_3$ to a solution of 0.100 g (0.400 mMol) of (**3**) in 10 ml of THF, was stirred at room temperature for 1 hour. All volatiles were then removed *in vacuo*, 10 ml of fresh THF was added and the solution filtered into 50 ml of pentane. This was cooled to −78° and the precipitate obtained was dried *in vacuo* to give 0.081 g (76%) of the white product (mp 237° (decomposition); *M/e* for P^+, 266.1344 ± 0.0013, calcd 266.1345).

$H_3BP(NMeNMe)_3P{=}NPh$, (**8**) To a solution of 0.615 g (1.88 mMol) of (**4**) in 25 ml of THF was added 3.0 ml of 1 *M* $THFBH_3$ solution *via* syringe. After stirring for 1 hour at room temperature, all volatiles were removed *in vacuo* to leave a white residue. The residue was taken up in 25 ml of fresh THF and filtered into 150 ml of pentane which caused a white solid to precipitate. This mixture was cooled to −78° and the solid filtered off and dried *in vacuo* to give 0.37 g (58%) of white product (mp 148–150° (decomposition); *m/e* for P^+, 341.1822 ± 0.0017, calcd 341.1818).

$MeC(CH_2NMe)_3P{=}O$, (**11**) This compound was synthesized by treating 3.60 ml (20.2 mMol) of the triamine precursor of (**2**)[9] and 8.43 ml (60.5 mMol) of NEt_3 in 40 ml of dry ether at 0° with a solution of 1.84 ml (20.0 mMol) of $POCl_3$ in 20 ml of dry ether. After addition, the mixture was stirred for 6 hours at room temperature and then filtered to remove amine hydrochloride. The clear filtrate was evaporated to a white residue which was sublimed at 60° (0.01 torr) to give 1.95 g (48%) of product. This compound was synthesized by Laube *et al.*[13] in 26% yield without the presence of NEt_3 in the reaction.

$O{=}P(NMeNMe)_3P{=}NPh$, (**13**) A solution of 0.58 g (1.8 mMol) of (**4**) in 15 ml of absolute ethanol was treated with 2 ml of 30% aqueous H_2O_2 at room temperature. After stirring for 20 minutes the flask was cooled to −10° which caused white crystals to form. These were recrystallized in 49% yield from hexane (mp 222°; *m/e* for P^+, 343.1433 ± 0.0017, calcd 343.1439).

DISCUSSION

BH_3 Stretching Frequencies of Adducts

The change in the asymmetric and symmetric stretching frequencies of the BH_3 upon constraint of the donor molecule has been shown to be a useful means of ordering phosphorus base strengths in phosphite esters, since increased planarity of the BH_3 group (induced by poorer donor character of the base) is associated with higher B—H stretching frequencies.[1] Given in Table I are the BH stretching frequency data for (**5**)–(**9**) along with data for three phosphite ester borane adducts (**14**)–(**16**) taken from earlier results.[1] The first feature of note in this table is that, as expected, the frequency relationships (**14**)

TABLE I
B—H stretching frequencies [a,b]

	$\nu BH(cm^{-1})$		
	asym	sym	wtd avge
$H_3BP(NMe_2)_3$ (**5**)	2372.0	2334.5	2359.5
$H_3BP(NMeCH_2)_3CMe$ (**6**)	2396.5	2350.5	2381.2
$H_3BP(NMeNMe)_3PO$ (**7**)	2408.0	2352.5	2389.5
$H_3BP(NMeNMe)_3PNPh$ (**8**)	2411.0	2357.0	2393.0
$H_3BP(NMeNMe)_3PBH_3$ (**9**)	2412.5	2360.5	2395.0
$H_3BP(OMe)_3$ (**14**)	2402	2362	2389
$H_3BP(OCH_2)_3CMe$ (**15**)	2415	2366	2399
$H_3BP\overbrace{(OCH_2)_2}^{O}CH$ (**16**)	2433	2380	2415

[a] Precise to ±0.5 cm^{-1} for (**5**)–(**9**) and to ±1 cm^{-1} for (**14**)–(**16**).
[b] Solvent was CCl_4.

> (**5**) and (**15**) > (**6**) suggest that aminophosphines are stronger bases than phosphite esters, given the same degree of constraint. The frequency trend (**5**) < (**6**) < (**7**) < (**8**) < (**9**) can be rationalized as follows. Constraint of (**5**) into the bicyclo[2.2.2]octane structures (**6**)–(**9**) brings the nitrogen lone pairs into an orthogonal relationship with the phosphorus lone pair in the case of (**6**)[14] and nearly so in (**7**)–(**9**) which probably posses structures very similar to those of (**12**)[15] and PhNP(NMeNMe)$_3$PNPh.[16] The phosphorus lone pair–nitrogen lone pair repulsions can be reduced by such an orthogonal relationship so that the polarizability of the phosphorus lone pair is decreased. The increasing frequency trend from(**6**) to (**7**)–(**9**) can therefore be ascribed to the larger electronegativity of the $(NMe)_3PZ$ group in (**7**)–(**9**) compared to $(CH_2)_3CMe$ in (**6**).[17]

While the increasing order in νBH values from (**7**) to (**8**) to (**9**) is opposite to that expected on electronegativity grounds, the observed trend may be associated with decreasing pi back donation in the order O > NPh > BH_3. While this postulate is reasonable for Z = O and NPh *versus* Z = BH_3, it is not obvious why the pi donor ability of oxygen might exceed that of the phenylimido group in (**7**) and (**8**), respectively, unless pi electron density in the P—N bond is preferentially delocalized onto the phenyl ring rather than onto the cage. Some support for this comes from the crystal structure determinations of (**12**)[15] and PhNP(NMeNMe)$_3$PNPh[16] wherein it can be seen that the P—O and P—N bonds are shortened by 17.0% and 15.5%, respectively, compared to the sum of the covalent radii. Calculations[18] based on an extension of the Letcher–Van Wazer semi-empirical theory of ^{31}P chemical shifts[19] also lead to a smaller N—P pi bond order for $PhNP(NMe_2)_3$ (0.53) compared to that calculated for the O—P bond in (**10**) (0.89) from analysis of its vibrational spectrum.[20] It is reasonable to suppose that a similar relationship holds for (**7**) and (**8**).

O=P Stretching Frequencies of Phosphoryl Compounds

Earlier we showed that constraint of phosphate esters (e.g., $OP(OMe)_3$ to $OP(OCH_2)_3CR$) produced higher O=P stretching frequencies.[1] The same phenomenon is observed from (**10**) (1210 cm^{-1}, solvent not specified)[20] to (**3**) (1283.0 cm^{-1}, CCl_4), (**11**) (1285.4 cm^{-1}, CCl_4) and (**12**) (1287.6 cm^{-1} or 1278.6 cm^{-1}, CCl_4). In both systems this result can arise from an increase in positive charge on the phosphorus[2] which augments O=P pi bonding.

Correlations of δ^1H with $^3J^{31}P^1H$

In a previous publication[21] it was determined that separate linear correlations exist between $^3J^{31}P^1H$ and δCH_2 in $YP(OCH_2)_3CMe$ where Y represents a series of sigma bonding acceptors or a series of acceptors which can also pi bond back to phosphorus. Figure 1 shows similar correlations for $^3JPNCH_2$ and δNCH_2 for $YP(NMeCH_2)_3CMe$. Table II contains the pertinent nmr data. The correlation coefficient for the line given by the sigma bounding groups Y = lone pair, H_3B, Ph_3C^+, Br^+ is

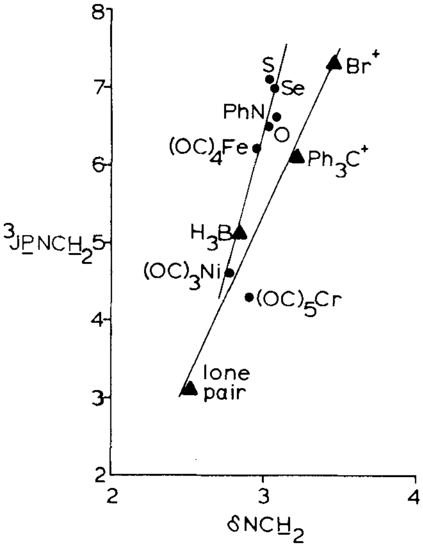


FIGURE 1 Plots of $^3J^{31}P^1H$ *versus* δNCH_2 for $YP(NMeCH_2)_3CMe$ where Y = sigma bonding groups (▲) and sigma accepting-pi donating groups (●). Y = $(OC)_5Cr$ has been excluded from the least squares line (see text).

TABLE II
^{1}H NMR parameters for derivatives of YP $(NMeCH_2)_3CMe$ in CD_3CN solution

Y	δNMe[a]	$^3JPNCH_3$[b]	δNCH_2[a]	$^3JPNCH_2$[b]	δCMe[a]
lone pair (**2**)	2.46	16.2	2.52	3.1	0.80
NPh	2.53	12.6	3.07	6.6	0.88
BH_3 (**6**)	2.50	14.1	2.83	5.1	0.86
O (**11**)	2.49	11.6	3.02	6.5	0.82
S	2.58	15.2	3.03	7.1	0.87
Se	2.62	16.0	3.06	7.0	0.89
$Br^+(Br^-)$[c]	2.79	16.9	3.45	7.3	1.00
$CPh_3^+(BF_4^-)$[c]	2.19	11.7	3.20	6.1	0.94
$Cr(CO)_5$	2.78	15.2	2.89	4.3	0.83
$Fe(CO)_4$	2.66	15.7	2.95	6.2	0.88
$Ni(CO)_2$ (**2**)	2.60	15.8	2.77	4.6	0.84

[a] In ppm downfield relative to TMS.
[b] Values precise to ±0.1 Hz.
[c] Counterion.

0.97 while that for the pi bonding groups Y = $(OC)_2$(**2**)Ni, $(OC)_4$Fe, O, PhN, Se, S is 0.91. Inclusion of Y = $(OC)_5$Cr brings the coefficient down to 0.78. The chromium complex may possess CH_2 protons which are shifted anomalously downfield owing to the diamagnetic anisotropy of the four carbonyl groups which lie *cis* to the cage ligand.

A rather poor correlation of δNCH_3 *versus* $^3JPNCH_3$ is found (Figure 2) for pi bonding groups Y = Se, $(OC)_3$(**3**)Ni, S, H_3B, NPh and O ($r^2 = 0.85$). Again inclusion of the Y = $(OC)_5$Cr point completely destroys the correlation ($r^2 = 0.45$) owing to the anomalously large downfield shifted NCH_3 protons. No correlation is apparent for the line given by Y = Br^+, lone pair, H_3B and Ph_3C^+ ($r^2 = 0.77$) unless the Y = lone pair point, for which $^3JPNCH_3$ seems inordinately high, is excluded ($r^2 = 1$). Aside from there being no obvious reason for such an exclusion of data, it seems odd that the Y = H_3B point lies between those possessing positive charges, namely, Y = Br^+ and Ph_3C^+. This does not occur in Figure 1 nor in the analogous correlation for $YP(OCH_2)_3CMe$.[21] The close proximity of the CH_3 protons to Y may at least in part be responsible for the poor correlations of $^3JPNCH_3$ *versus* δNCH_3.

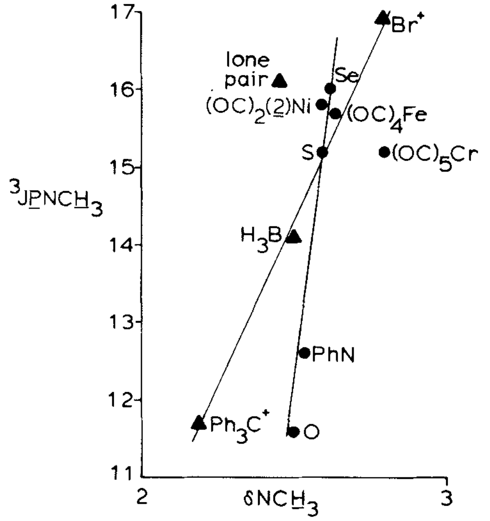


FIGURE 2 Plots of $^3J^{31}P^1H$ *versus* δNCH_3 for $YP(NMeCH_2)_3CMe$ where Y = sigma bonding groups (▲) and sigma accepting-pi donating groups (●). Y = $(OC)_5$Cr and lone pair have been excluded from the least squares lines (see text).

Dipole Moment Studies

The dipole moment data summarized in Table III suggest that constraint of (**1**) and (**10**) into the cages (**2**) and (**11**), respectively, does not give rise to substantial changes in the dipole moment. This contrasts the approximate doubling of the moments realized in going from $YP(OMe)_3$ to $YP(OCH_2)_3CMe$ which is attributable to the orientation of an esteratic oxygen lone pair density component along the C_{3v} axis of the cages.[21] In (**2**) and (**11**) only the relatively non polar $H_3C—N$ bond has a component along this axis and each of the three nitrogen lone pairs which are orthogonal to the axis have no contribution to μ. It is worthy of note that the dipole of (**4**) directs its positive end along the pseudo C_{3v} axis toward the trivalent phosphorus end. This conclusion is indicated by subtracting the contribution of the $P(NMe)_3$ end of (**4**), which is approximately given by μ of (**2**) (1.67 D), from μ of $MeC(CH_2NMe)_3P{=}NPh$ (4.90 D). The difference of 3.23 D is close to the moment observed for (**4**) (2.96

TABLE III
Dipole moments of aminophosphine compounds[a]

Compound	$\delta\varepsilon/\delta\chi$	$\delta\eta/\delta\chi$	P_0	μ^b	Solvent	Reference
$(Me_2N)_3P$ (**1**)	1.915	—[c]	29.94	1.21	C_6H_{12}	23
				1.46	C_6H_6	24
				1.56	C_6H_6	25
$MeC(CH_2NMe)_3P$ (**2**)	3.430	—[c]	53.62	1.62	C_6H_{12}	23
	3.486	0.020	57.12	1.67	$C_6H_5CH_3$	this work
			55.13	1.94	C_6H_6	24
$MeC(CH_2NMe)_3P{=}NPh$	29.95	0.172	490.5	4.90	$C_6H_5CH_3$	this work
$P(NMeNMe)_3P{=}NPh$ (**4**)	11.56	0.261	179.7	2.96	$C_6H_5CH_3$	this work
$(Me_2N)_3P{=}O$ (**10**)	17.36	—[c]	271.3	3.64	C_6H_{12}	23
				4.27	C_6H_6	24
				4.30	C_6H_6	25
				4.31	C_6H_6	26
				4.37	C_6H_6	27
				5.54	C_6H_6	28
$MeC(CH_2NMe)_3P{=}O$ (**11**)	24.52	—[c]	383.2	4.33	C_6H_{12}	23
	28.01	0.033	465.2	3.77	$C_6H_5CH_3$	this work

[a] All measurements made at 25.00 ± 0.05°.

[b] In Debyes. Values for this work and reference 23 are precise to ±0.05 D.

[c] Assumed to be zero.

D) as expected if the positive end of the dipole is near the trivalent phosphorus. This result may in part be responsible for the reluctance of $P(NMeNMe)_3P$ to react with more than one molecule of PhN_3.[11] A similar phenomenon was reported earlier by us for $P(OCH_2)_3P$.[22]

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