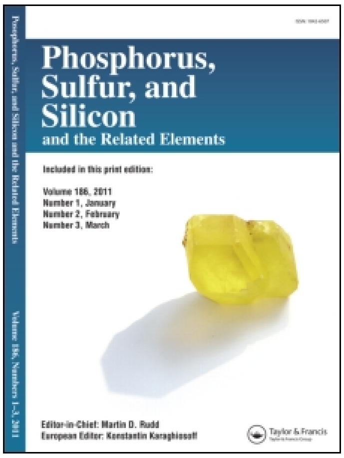

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^{31}P-^{31}P SPIN-SPIN COUPLINGS IN SYMMETRICAL AND UNSYMMETRICAL DERIVATIVES OF $P(NMeNMe)_3P$

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^{31}P–^{31}P SPIN-SPIN COUPLINGS IN SYMMETRICAL AND UNSYMMETRICAL DERIVATIVES OF $P(NMeNMe)_3P$

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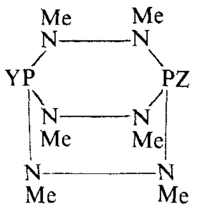
The syntheses and characterization of seven new unsymmetrical derivatives of the type $YP(NMeNMe)_3PZ$ are reported. Where Y = O or NPh: Z = S, Se, Br^+ and where Y = a lone pair, Z = Br^+ Also reported are the new symmetrical derivatives where Y = Z = $(OC)_5W$ or $(OC)_3Ni$ and the new monovalent cage cations $YP(NMeCH_2)_3CMe^+$ where Y = Ph_3C and Br. Conductivity and ^{31}P nmr evidence for the formulation of the phosphonium cations is presented. $^3J^{31}P^{31}P$ couplings, obtained directly from the ^{31}P nmr spectra of the unsymmetrical derivatives, are found to rise upon successively oxidizing the phosphorus atoms, and a rationale is offered. This coupling is also extracted from the ^{183}W and ^{77}Se satellite peaks in the ^{31}P spectra of the symmetrical derivatives where Y = Z = $(OC)_5W$ and Se, respectively.

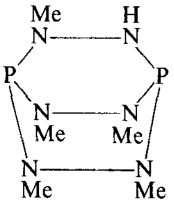
A self-consistent set of assignments of the ^{31}P chemical shifts is arrived at for $YP(NMeNMe)_3PZ$ compounds and the useful role of LIS reagents in analyzing their proton spectra is delineated. The ^{13}C nmr spectral parameters of these derivatives are also presented.

Prior to our characterization of (**1**) and (**2**),[1] the only reported compounds of the cage structure below have been symmetrical (i.e., Y = Z = lone pair[2] (lp), NPh,[3] $NP(O)(OPh)_2$,[1] $NP(O)Ph_2$,[3] BH_3,[2] O,[2] S,[2] Se[2]).



	Y	Z		Y	Z
(**1**)	lp	NPh	(**10**)	S	NPh
(**2**)	lp	N_3Ph	(**11**)	Se	NPh
(**3**)	lp	O	(**12**)	Br^+	NPh
(**4**)	H_3B	O	(**13**)	$(OC)_5W$	$W(CO)_5$
(**5**)	S	O	(**14**)	$(OC)_3Ni$	$Ni(CO)_3$
(**6**)	Se	O	(**15**)	Se	Se
(**7**)	Br^+	O	(**16**)	lp	lp
(**8**)	H_3B	NPh	(**17**)	lp	Br^+
(**9**)	O	NPh			

An attractive feature of the unsymmetrical derivatives (**3**)–(**12**) and (**17**) is that ^{31}P–^{31}P spin-spin couplings are readily obtained directly from the ^{31}P proton-decoupled nmr spectra. Although (**13**) and (**15**) are symmetrical products, they are isotopically unsymmetrical with respect to the nmr active ^{183}W (15%) and ^{77}Se (7.5%) nuclei, respectively. Thus the proton-decoupled ^{31}P nmr spectra of these systems represent the AB part of an ABX spectrum, from which ^{31}P–^{31}P couplings are directly accessible. Previous efforts to obtain ^{31}P–^{31}P couplings in the above cage system have been limited to (**16**) (~80 Hz based on a line shape analysis)[4] and a direct measurement from the ^{31}P nmr spectrum of (**18**) (32.0 Hz) which contains an unsymmetrical hydrazine bridge.[5]



(**18**)

In addition to a study of $^3J^{31}P^{31}P$ couplings in (**3**)–(**13**), (**15**) and (**17**), we report the synthesis of (**5**)–(**7**), (**10**)–(**14**), (**17**), $[MeC(CH_2NMe)_3PCPh_3]BF_4$ and $[MeC(CH_2NMe)_3PBr]Br$. Also described are ^1H nmr studies of these compounds in which LIS reagents have played an important role in assigning resonances. ^{13}C nmr parameters are reported for several of these systems.

EXPERIMENTAL

^{31}P and ^{13}C nmr spectra were obtained on solutions in 10 mm tubes with a Bruker HX-90 instrument operating at 36.434 MHz in the FT mode. The spectrometer was locked on the ^2H resonance of the deuterated solvent. The external standard for ^{31}P nmr work was 85% H_3PO_4 contained in a 1 mm capillary held coaxially in the sample tube by a PTFE vortex plug. The solvent carbons were used as internal standards for the ^{13}C spectra. Positive shifts are those downfield of the standard. ^1H nmr spectra were obtained on a Varian HA-100 spectrometer using TMS as an internal standard. Mass spectra were measured on an AEI MS902 high resolution spectrometer. Infrared spectra were recorded on a Beckman IR 4250 spectrophotometer using a polystyrene standard for calibration. Conductivity measurements were made on $\sim 10^{-2}$ molar solutions in MeCN at room temperature using an Industrial Instruments RC-1632 conductivity bridge operated at 1000 Hz.

Compounds (**1**),[1] (**2**),[1] (**3**),[6] (**4**),[6] (**8**),[6] (**9**),[6] (**15**),[2] (**16**),[2] $[BrP(NMe_2)_3]Br$,[7] $[Ph_3CP(NMe_2)_3]BF_4$,[8] $PhNP(NMeNMe)_3PNPh$,[1] $(PhO)_2P(O)NP(NMeNMe)_3PNP(OPh)_2$,[1] $Ph_2P(O)NP(NMeNMe)_3PN(O)Ph_2$,[1] $H_3BP(NMeNMe)_3PBH_3$,[6] $OP(NMeNMe)_3PO$[2] and $SP(NMeNMe)_3PS$[2] were prepared as reported elsewhere.

$S{=}P(NMeNMe)_3P{=}O$, (**5**) A mixture of 0.198 g (0.784 mMol) of (**3**) and 0.0467 g (1.46 mg Atoms) of sublimed sulfur in 10 ml of toluene was refluxed for 8 hours. The solution was decanted from the unreacted sulfur and cooled to room temperature whereupon 50 ml of pentane was added to cause precipitation. After cooling the mixture to −78°, the solid was filtered, washed with pentane and dried *in vacuo* to give 0.125 g (56%) of pure white product subliming at 260° without melting (*m/e* for P^+, 284.0745 ± 0.0014, calcd 284.0738).

$Se{=}P(NMeNMe)_3P{=}O$, (**6**) A mixture composed of 0.46 g (1.8 mMol) of (**3**) and 0.20 g (2.6 mg Atoms) of red selenium in 15 ml of toluene was heated to 80° for 24 hours. The hot mixture was filtered and the residue was extracted with 10 ml of $CHCl_3$ and filtered. White crystals formed in the toluene filtrate as it cooled and the $CHCl_3$ was removed under vacuum to give a white residue. The two solids were combined and recrystallized from 15 ml of boiling toluene at −78° to give 0.47 g (83%) of the white product which sublimed at 255° without melting (*m/e* for P^+, 332.006 ± 0.020, calcd 332. 0182).

$[BrP(NMeNMe)_3PO]Br$, (**7**) Equimolar equivalents of (**3**) dissolved in $CDCl_3$ or CD_3CN and Br_2 dissolved in CCl_4 were combined under dry N_2 and used immediately (owing to hydrolytic instability) for characterization by ^1H and ^{31}P nmr spectroscopy (see Discussion).

$S{=}P(NMeNMe)_3P{=}NPh$, (**10**) A mixture of 0.475 g (1.45 mMol) of (**1**) and 0.70 g (2.2 mg Atoms, 50% excess) of sublimed sulfur in 15 ml of toluene was heated to reflux for 3 hours. The hot solution was decanted from the rubbery unreacted sulfur and cooled to room temperature whereupon 50 ml of pentane was added to cause precipitation. The precipitate was recrystallized from hexane to give 0.275 g (53%) of the white product (mp 224°; *m/e* for P^+, 359.1198 ± 0.0018, calcd 359.1211).

$Se{=}P(NMeNMe)_3P{=}NPh$, (**11**) A mixture of 0.7036 g (2.151 mMol) of (**1**) and 0.18 g (2.3 mg Atoms) of red selenium in 10 ml of dry benzene was refluxed for 17 hours and then filtered while hot. Upon cooling, a solid crystallized out which was washed with ether and dried *in vacuo* to give 0.665 g (76%) of product (mp 228–230°; *m/e* for P^+, 407.0585 ± 0.0017, calcd 407.0655).

$[BrP(NMeNMe)_3P{=}NPh]Br$, (**12**) This compound was prepared and characterized analogously to (**7**).

$(OC)_5WP(NMeNMe)_3PW(CO)_5$, (**13**) A mixture of 0.86 g (3.6 mMol) of (**16**) and 4.25 g (7.31 mMol) of $NEt_4[W(CO)_5I]$[9] suspended in 50 ml of CH_2Cl_2 was treated with a solution of 2.41 g (12.4 mMol) of $AgBF_4$ in 20 ml of nitromethane at room temperature. The suspension immediately changed from bright yellow to dark brown. Stirring was continued for 3 hours and then the volatiles were removed under vacuum. The residue was extracted twice with 40 ml portions of boiling toluene. The toluene was removed under vacuum and the residue was extracted with 40 ml of heptane at 95° to give a clear yellow solution. Cooling this solution to −78° caused precipitation of 0.32 g (10%) of golden yellow solid which was only slightly soluble in common solvents.

$(OC)_3NiP(NMeNMe)_3PNi(CO)_3$, (**14**) A solution of 1.10 g (4.66 mMol) of (**16**) in 10 ml of toluene was added dropwise to a solution of 1.21 ml (9.35 mMol) of $Ni(CO)_4$ in 10 ml of toluene at room temperature over a period of 5 minutes. Gas evolution was vigorous and ceased after 15 minutes. The clear colorless solution was stirred for 1 hour and then cooled to −78° which caused a solid to precipitate. This was filtered, washed with cold pentane and dried *in vacuo* to give 1.94 g (79%) of the tan product.

$[P(NMeNMe)_3PBr]Br$ (**17**) To a solution of 1.49 g (6.29 mMol) of (**16**) in 25 ml of CCl_4 was added 6.2 ml of a 1.0 *M* Br_2/CCl_4 solution (6.2 mMol Br_2) at 0°. As each drop of bromine solution was added its color was discharged and a bright yellow solid formed. The mixture was stirred for 10 minutes after all the bromine had been added and then the solid was filtered off, washed three times with cold ether and dried *in vacuo* to give 2.35 g (96%) of cream colored solid which was characterized by its ^1H and ^{31}P nmr spectra (see Discussion).

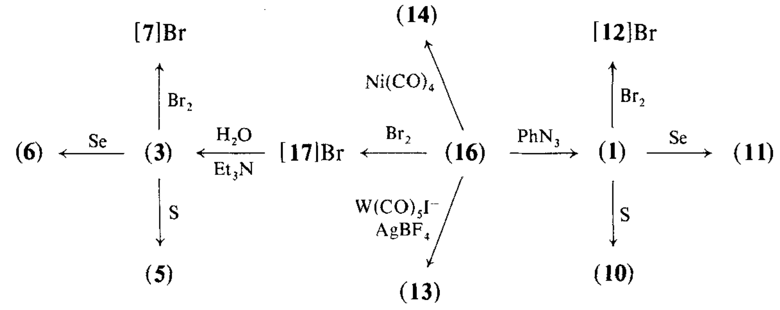
$[MeC(CH_2NMe)_3PCPh_3]BF_4$ To a solution of 1.54 g (4.65 mMol) of triphenylmethyl fluoroborate in 20 ml of CH_2Cl_2 was added 0.83 ml (4.7 mMol) of $MeC(CH_2NMe)_3P$ dropwise at room temperature. The initially dark turbid solution became a clear golden color. After stirring for ½ hour addition of 50 ml of ether caused precipitation of a tan solid. This was filtered, washed three times with ether and dried *in vacuo* to give 2.09 g (87%) of product which was characterized by its ^1H and ^{31}P nmr spectra (see Discussion).

$[MeC(CH_2NMe)_3PBr]Br$ A solution of 1.00 ml (5.60 mMol) of $MeC(CH_2NMe)_3P$ in 20 ml of CCl_4 was cooled in an ice bath and 5.6 ml of a 1.0 *M* Br_2/CCl_4 solution (5.6 mMol Br_2) was added dropwise with vigorous stirring. The bromine color was immediately discharged and a light yellow precipitate formed. After stirring for 10 minutes following the addition, the solid was filtered off, washed twice with cold ether and dried *in vacuo* to give 1.92 g (100%) of cream colored product (mp 163° (decomposition)). The product was further characterized by ^1H and ^{31}P spectroscopy (see Discussion).

DISCUSSION

Syntheses and Characterization

The reactions used to make the new diphosphorus cages reported herein are summarized in Scheme 1. Particularly noteworthy are the bromine reactions which give rise to the neutral monoxide (**3**) and the cations (**7**), (**12**) and (**17**). Although the synthesis for the monoxide (**3**) was described elsewhere,[6] it is of interest to mention here that attempts to produce this compound with other reagents such as N_2O_4, *m*-



Scheme 1

TABLE I
^{31}P NMR chemical shifts for aminophosphine salts and their precursors[a]

Compound	Chemical shift		
	$\delta P(III)$	δP^+	$\delta P(V)$
$(Me_2N)_3P$:	120.9		
$[(Me_2N)_3P{-}Br]Br$		47.0	
$[(Me_2N)_3P{-}CPh_3]BF_4$		52.4	
$MeC(CH_2NMe)_3P$:	84.0		
$[MeC(CH_2NMe)_3P{-}Br]Br$		53.1	
$[MeC(CH_2NMe)_3P{-}CPh_3]BF_4$		43.6	
$:P(NMeNMe)_3P$: (**16**)	106.9		
$[:P(NMeNMe)_3P{-}Br]Br$ (**17**)	113.7	14.4	
$:P(NMeNMe)_3P{=}NPh$ (**1**)	95.9		−3.1
$[Br{-}P(NMeNMe)_3P{=}NPh]Br$ (**12**)		23.1[b]	−16.2[b]
$:P(NMeNMe)_3P{=}O$ (**3**)	94.9		9.8
$[Br{-}P(NMeNMe)_3P{=}O]Br$ (**7**)		26.1	7.3

[a] Recorded in CD_3CN at 0° unless noted otherwise.
[b] $CDCl_3$ solvent at 0°.

$ClC_6H_4CO_3H$ and Me_3NO gave only uncharacterized oils. Efforts to convert (**1**) and (**3**) using PhNCO or 3-pentanone under conditions which convert R_3PNR to $R_3P{=}O$[10] also failed.

Like $P(NMe_2)_3$,[7] the caged aminophosphines (**1**), (**3**), (**16**) and $MeC(CH_2NMe)_3P$ give 1 : 1 electrolytes of the type $[BrP(NR_2)_3]^+Br^-$. Thus, for example, $[BrP(NMe_2)_3]Br$, [**17**]Br and $[MeC(CH_2NMe)_3PBr]Br$ in MeCN give room temperature conductivities of 140, 152 and 125 mhos cm^{-1} l Mol^{-1}, respectively, which compare favorably with 145 mhos cm^{-1} l Mol^{-1} for Et_4NI in the same solvent. Recorded in Table I are ^{31}P nmr chemical shifts for the bromine adducts and related compounds. By comparing the δP^+ shifts of $[BrP(NMe_2)_3]Br$ and $[Ph_3CP(NMe_2)_3]BF_4$, the ionic formulation of the former salt in a polar solvent is substantiated and a similar argument can be applied to the $MeC(CH_2NMe)_3P$ analogs. Since the shifts of (**7**) and (**12**) lie in the same region as the 1 : 1 electrolyte (**17**), it is likely that they too are ionic in the solvents indicated. Earlier, $[BrP(NMe_2)_3]Br$ has been metathesized to its BPh_4 – 7 and PF_6 – 11 salts. Metathesis of this compound and $[MeC(CH_2NMe)_3PBr]Br$ with $AgBF_4$ in CD_3CN gave solutions which exhibited δP^+ values very close to that of their respective bromide salts (47.2 and 52.8 ppm). These results further confirm the ionic nature of the bromine reaction products described here.

^{31}P–^{31}P Couplings

With the exception of (**13**) and (**17**), in Table II, there appears to be a rise in $^3J^{31}P^{31}P$ in progressing from (**16**) wherein both phosphorus atoms are tricoordinate, to (**1**)–(**3**) wherein one three coordinate and one four coordinate phosphorus is present, to (**4**)–(**12**) and (**15**) in which both phosphorus atoms are four coordinate. Since there is no compelling reason to invoke a through space (across-the-cage) ^{31}P–^{31}P coupling mechanism in

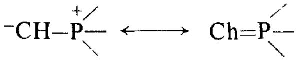
TABLE II
^{31}P nmr parameters for derivatives of $P(NMeNMe)_3P$[a]

Compound	Chemical shifts	^3JPP[b]
$:P(NMeNMe)_3P:$ (**16**)	$107.4^c(109)^d$	32.0^e
$:P(NMeNMe)_3P{=}N{-}N{=}NPh$ (**2**)	102.0 25.4	74.4^f
$(OC)_3Ni($**16**$)Ni(CO)_3$ (**14**)	131.2	—
$(OC)_5W($**16**$)W(CO)_5$ (**13**)	134.6	75^g
$:P(NMeNMe)_3P{=}NPh$ (**1**)	96.8 −1.8	78.2^f
$:P(NMeNMe)_3P{=}O$ (**3**)	96.1 5.6	84.3
$H_3B:P(NMeNMe)_3PBH_3$	$103.7(101.5)^e$	—
$H_3B:P(NMeNMe)_3P{=}NPh$ (**8**)	98.6 −6.1	99.9
$H_3B:P(NMeNMe)_3P{=}O$ (**4**)	100.1 9.5	101.0
$PhN{=}P(NMeNMe)_3P{=}NPh$	$-6.0\ (-6.6)^h$	—
$O{=}P(NMeNMe)_3P{=}NPh$ (**9**)	9.0 −6.8	102.0
$S{=}P(NMeNMe)_3P{=}O$ (**5**)	66.2 8.8	105.3
$S{=}P(NMeNMe)_3P{=}NPh$ (**10**)	65.6 −6.7	106.5
$(PhO)_2P(O)N{=}P(NMeNMe)_3P{=}NP(O)(OPh)_2$	$1.0\ -13.9^j$	107.5^f
$Se{=}P(NMeNMe)_3P{=}O$ (**6**)	67.3 8.0	107.6
$Se{=}P(NMeNMe)_3P{=}NPh$ (**11**)	67.0 −7.3	107.6
$[Br{-}P(NMeNMe)_3P{=}NPh]Br$ (**12**)	23.1 −16.2	109.8
$[Br{-}P(NMeNMe)_3P{=}O]Br$ (**7**)	23.6 6.9	110.4
$Ph_2P(O)N{=}P(NMeNMe)_3P{=}NP(O)Ph_2$	$2.5^i\ 12.2^j$	110.5^f
$O{=}P(NMeNMe)_3P{=}O$	$8.9\ (8.6)^k$	—
$S{=}P(NMeNMe)_3P{=}S$	66.5^j	—
$Se{=}P(NMeNMe)_3P{=}Se$ (**15**)	67.0	113.6^g
$[:P(NMeNMe)_3P{-}Br]Br$ (**17**)	112.7 16.1	132.1

[a] Recorded in $CDCl_3$ unless noted. [b] Values precise to ±1.1 Hz except for (**13**) (±5 Hz). [c] C_6H_6 solution. [d] In C_6H_6 (Ref. 2). [e] Assumed to be same as for (**18**) (Ref. 5). [f] Ref. 1. [g] Obtained from ITRCAL-analyzed spectrum (see Ref. 1). [h] In $CHCl_3$ (Ref. 3). [i] Bridgehead phosphorus. [j] Exocyclic phosphorus. [k] CH_2Cl_2 solution.

compounds such as these,[12] it is assumed in the following discussion that coupling occurs through the bonds of the three bridging hydrazino groups. The general rise in coupling upon binding the phosphorus atoms in (**16**) to a fourth substituent can be understood in terms of the increased s character in the P—N bonds and the higher positive charge on phosphorus expected from coordination to a fourth group. It is not apparent why (**13**) and (**17**) are out of line, however.

Where one of the phosphorus substituents is kept constant, e.g., (**1**), (**8**)–(**12**) and (**3**), (**4**)–(**7**), the trend in $^3J^{31}P^{31}P$ for both sets of compounds as a function of the other phosphorus substituent is lp < H_3B < O < S < Se < Br^+. The general progression lp < H_3B < chalcogen < Br^+ seems quite reasonable since phosphorus charge and P—N s character are expected to rise with substituent electronegativity. The order among the chalcogens seems odd at first glance, since it is the reverse of that expected on electronegativity grounds. The dominant effect here may be an increasing contribution from the dipolar resonance form shown below which may be expected from a decrease in pi bonding O < S < Se.[13] This effect can also be seen in comparing the couplings of (**6**) and (**15**). Previously we observed this phenomenon in derivatives of $P(OCH_2)_3P$ wherein $^3J^{31}P^{31}P$ for $OP(OCH_2)_3PO$ (139.1 Hz) is less than that for $SP(OCH_2)_3PO$ (151.3 Hz).[12] The electronegativity effect would again appear to be in evidence for the series in Table II where one phosphorus is maintained in the tricoordinate form (i.e., (**16**), (**2**), (**1**), (**3**) and (**17**). Thus $^3J^{31}P^{31}P$ increases in the order lp < N_3Ph < NPh < O < Br^+ for the substituents on the four-coordinate phosphorus. The order of the nitrogen and oxygen substituents can not be taken very seriously, however, because the couplings are about equal in the pairs (**4**), (**8**); (**5**) (**10**); (**6**), (**11**) and (**7**), (**12**).



$$^-CH{-}\overset{+}{P}{<} \longleftrightarrow Ch{=}P{<}$$

The negative sign of $^3J^{31}P^{31}P$ in $P(OCH_2)_3P$ is known to reverse upon coordination of either or both phosphorus atoms to a fourth group.[12] While it is likely that $^3J^{31}P^{31}P$ is also positive in the derivatives of (**16**), the sign of this coupling in (**16**) is presently unknown.

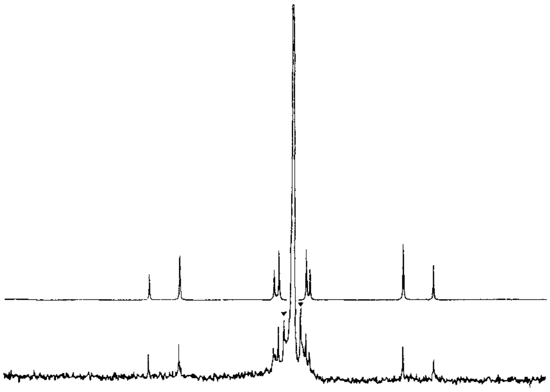


FIGURE 1 Proton decoupled ^{31}P nmr spectrum of Se=P(NMeNMe)$_3$P=Se (**13**). The computer generated spectrum illustrating the effect of $^{3}J^{31}P^{31}P$ coupling is displayed above the experimental spectrum. The peaks marked with ▼ are spinning sidebands.

The interesting proton decoupled ^{31}P FT nmr spectrum of the diselenide (**15**) shown in Figure 1 exemplifies the A branch of an ABX spectrum due to $^{77}Se^{31}P(NMeNMe)_3{}^{31}PSe$ superimposed on the A_2 spectrum arising from $Se^{31}P(NMeNMe)_3{}^{31}PSe$; the AA′XX′ spectrum due to $^{77}Se^{31}P(NMeNMe)_3{}^{31}P^{77}Se$ is expected to be more than an order of magnitude less intense. The presence of the first species permits the determination of $^{3}J^{31}P^{31}P$. The computer simulated spectrum shown in Figure 1 fits the experimental one with an rms error of 9.3×10^{-4} Hz and it also reveals the selenium isotope influence in the chemical shifts of $\delta^{31}P(^{77}Se)$ (66.2) and $\delta^{31}P(Se)$ (67.0 ppm).

The proton decoupled ^{31}P FT nmr spectrum of the ditungsten complex (**13**) is similar to that of (**15**) owing to the 14.3% abundance of ^{183}W ($I = \frac{1}{2}$). The rms value for the simulated spectrum is higher however (2.64 Hz) so that the $^{1}J^{31}P^{183}W$ and $^{3}J^{31}P^{31}P$ couplings for (**13**) are probably only accurate to ±5 Hz. The $^{183}W^{31}P$ coupling for (**13**) (338 Hz) compares favorably with the value obtained for $(OC)_5WP(NMeCH_2)_3CMe$ (320.7 Hz) and that obtained earlier for $(OC)_5WP(NMeCH_2)_3C$-*n*-C_5H_{11} (318 Hz).[14]

^{31}*P Chemical Shift Assignments*

The assignments of δ^{31}P in Table II are made straightforward by comparing the chemical shifts of (**16**) with those of all other derivatives in which a phosphorus lone pair is present. In this way ^{31}P chemical shift ranges for the four coordinate phosphorus substituents can be obtained. Applying this information to the remaining compounds renders all the assignments self-consistent.

^{1}*H Chemical Shift Assignments*

Lanthanide induced shift (LIS) reagents facilitate the ^{1}H nmr spectral analysis of unsymmetrical derivatives of (**16**) such as (**3**) because of the greater affinity of the LIS reagent for the phosphoryl oxygen

TABLE III

^{1}H nmr spectral data for unsymmetrical derivatives $(X)P_a(NMe_aNMe_b)_3P_b(Y)$[a]

Compounds		Proton Chemical shifts[b]		Coupling constants[c]			
X	Y	δMe_a	δMe_b	$^{3}J^{31}P_a{}^{1}H_a$	$^{3}J^{31}P_b{}^{1}H_b$	$^{4}J^{31}P_a{}^{1}H_b$	$^{4}J^{31}P_b{}^{1}H_a$
lone pair	Br^{+}[d] (**17**)	3.30	3.12	10.3	12.6	0[e]	2.8
lone pair	O[f] (**3**)	2.77	2.73	15.1	9.7	0[e]	1.7
lone pair	N_3Ph (**2**)	2.90	2.94	14.5	10.3	0[e]	1.5
lone pair	NPh (**1**)	2.86	2.85	14.8	10.4	0[e]	1.6
O	NPh (**9**)	2.95	2.92	9.5	10.1	1.6	1.6
S	NPh (**10**)	3.01	2.92	11.4	9.8	1.6	1.6
Se	NPh (**11**)	3.05	2.95	12.0	9.6	1.5	1.6
H_3B	NPh (**8**)	2.93	2.90	12.1	9.8	0[e]	1.6
S	O (**5**)	2.97	2.91	11.0	9.1	1.4	1.5
Se	O (**6**)	3.03	2.94	12.0	9.1	1.5	1.7
H_3B	O (**4**)	2.91	2.88	11.9	9.4	0[e]	1.6

[a] Recorded in $CDCl_3$ unless noted otherwise.
[b] See text for assignments.
[c] Values precise to ±0.2 Hz.
[d] Counterion is Br^-.
[e] Undetectably small.
[f] In CCl_4.

TABLE IV
^1H nmr spectral data for $P(NMeNMe)_3P$ and its symmetrical derivatives[a]

Compound	Chemical shifts		Coupling constants[c]	Reference
	δNMe	δPh[b]		
$P(NMeNMe)_3P$ (**16**)	2.83		15.0	this work
	2.78[d]		15.2	5
$PhN{=}P(NMeNMe)_3P{=}NPh$	2.98	7.05	11.0	this work
	2.98	6.93	11.0	3
$(PhO)_2P(O)N{=}P(NMeNMe)_3P{=}NP(O)(OPh)_2$	2.85	7.24	12.0	this work
$Ph_2P(O)N{=}P(NMeNMe)_3P{=}NP(O)Ph_2$	2.92	—[e]	12.0	this work
	2.93	—[f]	12.0	3
$H_3BP(NMeNMe)_3PBH_3$[g]	2.87[c]		12.6	2
$O{=}P(NMeNMe)_3P{=}O$	2.88[h]		11.0	2
$S{=}P(NMeNMe)_3P{=}S$	2.96[h]		12.8	2
$Se{=}P(NMeNMe)_3P{=}Se$ (**15**)	2.95[h]		12.8	2

[a] Recorded in $CDCl_3$ solution except where noted.
[b] Resonances are multiplets and centers are reported.
[c] $|^3J^{31}P^1H + {}^4J^{31}P^1H|$ for the pseudotriplet. Values for the present work are precise to ±0.2 Hz.
[d] In C_6H_6 solution.
[e] Two multiplets centered at 7.38 and 7.78 ppm.
[f] Three multiplets centered at 7.35, 7.68 and 7.83 ppm.
[g] The BH_3 protons were not observed.
[h] In CH_2Cl_2.

than for the trivalent phosphorus lone pair.[15] The proton nmr data for the unsymmetrical derivatives of (**16**) are collected in Table III while those of (**16**) and some of its symmetrical derivatives are listed in Table IV. Incremental addition of either Eu or $Pr(dpm)_3$ to a CCl_4 solution of $O{=}P(NMeCH_2)_3CMe$ produces larger shifts in the NMe protons than in the CH_2 protons because of the closer proximity of the former atoms to the LIS reagent. A similar experiment with (**3**) showed that the larger NMe proton resonance (the doublet in Figure 2) moves upfield more rapidly than the smaller one (the doublet of doublets). The doublet is therefore assigned to the phosphoryl phosphorus. It is seen that while both phosphorus nuclei couple to the NMe protons nearest them, the coupling of the P(V) nucleus to the more distant protons ($^4J^{31}P^1H$) must be near zero. The $^3J^{31}P^1H$ values obtained for (**3**) in Table III are in good agreement with those derived from (**16**) and $OP(NMeNMe)_3PO$ in Table IV. The latter compounds both exhibit a pseudotriplet in the ^1H nmr spectrum in which the separation of the outermost peaks is $|^3J^{31}P^1H + {}^4J^{31}P^1H|$. The 15.0 Hz separation for (**16**) and the 15.1 Hz $^3J^{31}P^1H$ coupling for the P(III) phosphorus of (**3**) suggests that $^4J^{31}P(III)^1H$ is near zero in (**3**). This result disagrees with that of other workers[5] who found that a best fit for the spectrum of (**16**) occurred when $^3J^{31}P^1H$ is 12.8 Hz and $^4J^{31}P^1H$ is 2.4 Hz.

For (**3**), the sum $|^3J^{31}P^1H + {}^4J^{31}P^1H|$ for the P(V) phosphorus is 11.4 Hz which closely matches that obtained from the outermost peak separation in the spectrum of $OP(NMeNMe)_3PO$. This indicates that both couplings are of the same sign.

A similar analysis of the ^1H nmr parameters of (**1**) predicts a $|^3J^{31}P^1H + {}^4J^{31}P^1H|$ value of 14.8 Hz for (**16**) and 12.0 Hz for $PhNP(NMeNMe)_3PNPh$ in excellent agreement with the respective magnitudes of 15.0 and 12.0 Hz observed.

By assuming that the H_3B group confers more P(III) than P(V) character on the adducted phosphorus (i.e., $^4J^{31}P^1H$ is very small) the ^1H nmr spectral assignments for (**4**) and (**8**) in Table III can be made. The assignments in the spectrum of (**2**) were made on the basis of its analogy with (**1**).

Spectral assignments for the unsymmetrical bicyclic compounds in which both phosphorus atoms are P(V) (i.e. (**5**), (**6**) and (**9**)–(**11**)) are not as straightforward since the $^4J^{31}P^1H$ couplings are nearly the same size. The somewhat more constant values assigned to the $^3J^{31}P_b{}^1H_b$ coupling in Table III for these compounds are in accord with the expectation that smaller electronic changes occur at the PNPh or PO phosphorus than for $^3J^{31}P_a{}^1H_a$ associated with the phosphorus which is bonded to different chalcogens. Moreover, the slight increase in $^3J^{31}P_a{}^1H_a$ in the order O < S < Se is consistent with the concommitant increase in $^3J^{31}P^{31}P$ dis-

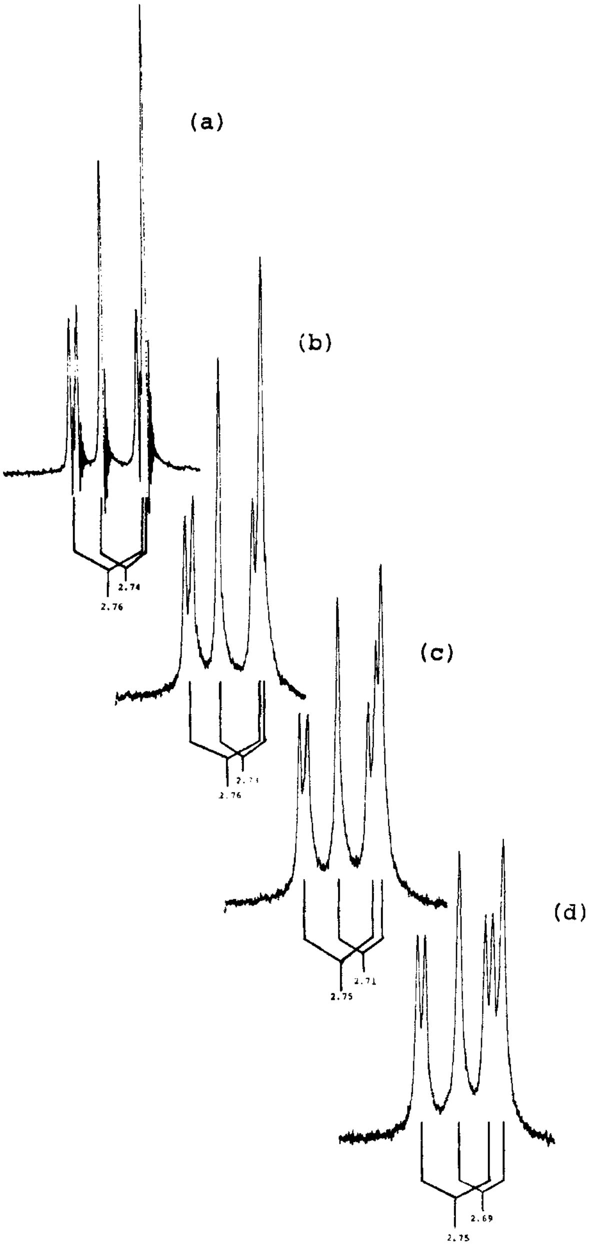


FIGURE 2 LIS effects on the proton spectrum of $P(NMeNMe)_3P{=}O$ (**3**) upon addition of incremental amounts of the upfield shift reagent $Pr(dpm)_3$ progressing from (a) containing no LIS to (d).

cussed earlier which was attributed to a rise in the polar character of the phosphorus–chalcogen bond. This rationale also can account for the slightly increasing downfield chemical shifts for δMe_a of these compounds in the order $O < S < Se$ (Table III). It may be noted that an increasing trend in $^3J^{31}P^1H$ has also been observed for $ChP(NMe_2)_3$ in the order $O < S < Se < Te$.[2]

^{13}C nmr Spectra

In Table V the decrease in $^2J^{31}P^{13}C$ observed by others[16] when $P(NMe_2)_3$ is oxidized is paralleled by the sum of the couplings $|^2J^{31}P^{13}C + {}^3J^{31}P^{13}C|$ from (**16**) to $OP(NMeNMe)_3PO$ and $PhNP(NMeNMe)_3PNPh$. The latter couplings also permit the assignment of the larger coupling in the ^{13}C nmr spectra of (**1**) and (**3**) to $^2J^{31}P(III)^{13}C$ and the smaller one to $^2J^{31}P(V)^{13}C$.

Low temperature nmr studies of P(III) compounds show that $^2J^{31}P^{13}C$ is large and positive for carbons *cis* to the phosphorus lone pair and small and negative for *trans* carbons.[17] While a sizeable $^2J^{31}P^{13}C$ coupling of 12.8 Hz is observed for (**16**) wherein all the methyls are *cis* to phosphorus lone pairs, none is detected for the *cis* carbons of $P(NMeCH_2)_3CMe$ and a 3.9 Hz coupling is seen for the *trans* carbons. Moreover, the *cis* $^2J^{31}P^{13}C$ couplings range from 2.9–4.4 Hz for the P(V) phosphorus in (**1**), (**3**), $OP(NMeNMe)_3PO$ and $PhNP(NMeNMe)_3PNPh$ while remaining undetectably small in $ChP(NMeCH_2)_3CMe$ (Ch = O, S, Se).

Relatively large bridgehead atom couplings given by $^3J^{31}P^{13}C$ in Table VI are observed which may be attributable to a favorable coupling path afforded by the *cis*-vicinal relationship of the coupling atoms in the cage. This idea is supported by similarly large couplings seen for $P(OCH_2)_3CMe$ (22.8 Hz),[18] $OP(OCH_2)_3CMe$ (38.2 Hz),[18] and $OP(CH_2CH_2)_3CH$ (47 Hz).[19] Furthermore, the analogous couplings in $P(OEt)_3$ and $OP(OEt)_3$ in which free rotation occurs are only +4.9 and +6.8 Hz, respectively.[20] No $^4J^{31}P^{13}C$ couplings were seen for the compounds in Table VI. Whereas this is also the case for $OP(OCH_2)_3CMe$,[18] a 4.4 Hz coupling was detected for $P(OCH_2)_3CMe$.[18]

Using the value of 32.0 Hz discussed earlier for $^3J^{31}P^{31}P$ in (**16**), the pseudo-triplet proton decoupled ^{13}C nmr spectrum of this compound (which represents the X part of an AA′X system) could be duplicated by computer analysis (ITRCAL),[1] assuming that the outer peak separation $|^2J^{31}P^{13}C + {}^3J^{31}P^{13}C| \simeq {}^2J^{31}P^{13}C$ (i.e., the more distant coupling is zero). The value of $^2J^{31}P^{13}C$ so obtained (12.8 Hz) is reasonable since the proton decoupled ^{13}C nmr spectra of (**1**) and (**3**) consist of two doublets from which it can be determined by ^{13}C chemical shift comparisons of (**16**), (**1**), $PhNP(NMeNMe)_3PNPh$, (**3**) and $OP(NMeNMeP)_3O$ that $^2J^{31}P^{13}C$ for P(III)

TABLE V
^{13}C nmr spectral data for $P(NMe_2)_3$ and $P(NMeNMe)_3P$ and their derivatives

Compound	Chemical shifts[a] $\delta^{13}C$	Coupling constants	Solvent
$(Me_2N)_3P$	—	+19.15 (±0.05)[b]	neat[c]
$(Me_2N)_3P{=}O$	—	+3.4 (±0.1)[b]	neat[c]
$(Me_2N)_3P{=}S$	—	+3.3 (±0.05)[b]	neat[c]
$(Me_2N)_3P{=}Se$	36.6	3.9 (±0.5)[b]	$CDCl_3$
$P(NMeNMe)_3P$ (**16**)	37.7	12.8 (±1.0)[d]	C_6D_6
$PhN{=}P(NMeNMe)_3P{=}NPh$	37.0	4.4 (±0.5)[d]	$CDCl_3$
$O{=}P(NMeNMe)_3P{=}O$	36.3	4.4 (±0.5)[d]	$CDCl_3$
$P(NMeNMe)_3P{=}NPh$ (**1**)	37.8[e]	9.8 (±1.0)[b]	$CDCl_3$
	35.5[f]	3.9 (±1.0)[b]	
$P(NMeNMe)_3P{=}O$ (**3**)	37.9[e]	9.8 (±1.0)[b]	$CDCl_3$
	36.3[f]	2.9 (±1.0)[b]	

[a] Referenced relative to TMS.
[b] Doublet due to $^2J^{31}P^{13}C$.
[c] Ref. 16.
[d] Pseudotriplet. Coupling reported is separation of outermost peaks for the Me carbon.
[e] Carbons closest to P(III).
[f] Carbons closest to P(V).

TABLE VI
^{13}C nmr spectral data for $P(NMeCH_2)_3CMe$ and its derivatives[a]

Compound	NMe carbon[b]		NCH_2 carbon[b]		Bridgehead carbon[b]		Methyl carbon[b] $\delta^{13}C$
	$\delta^{13}C$	$^2J^{31}P^{13}C$	$\delta^{13}C$	$^2J^{31}P^{13}C$	$\delta^{13}C$	$^3J^{31}P^{13}C$	
$P(NMeCH_2)_3CMe$	34.8	—[c]	61.2	3.9	40.0	25.9	22.7[d]
$O{=}P(NMeCH_2)_3CMe$	35.3	—[c]	62.9	—[c]	33.5	30.8	20.4
$S{=}P(NMeCH_2)_3CMe$	37.3	—[c]	62.5	2.9	33.3	25.4	21.2
$Se{=}P(NMeCH_2)_3CMe$	38.6	—[c]	62.4	3.9	34.1	24.4	21.5

[a] The solvent used was $CDCl_3$ except for $P(NMeCH_2)_3CMe$ where it was C_6D_6. Coupling constants are precise to ±0.5 Hz.
[b] Assignments were based on the gated decoupled spectrum of $P(NMeCH_2)_3CMe$.
[c] Insufficient resolution. Coupling probably near zero.
[d] There is no $^4J^{31}P^{13}C$ coupling observed.

is 9.8 Hz in (**1**) and (**3**), while for P(V) this value is 3.9 and 2.9 Hz, respectively.

From Table II it is seen that a reasonable value for $^3J^{31}P^{31}P$ in $PhNP(NMeNMe)_3PNPh$ and $OP(NMeNMe)_3PO$ is about 100 Hz. Using this number for $^3J^{31}P^{31}P$ along with $^2J^{31}P^{13}C = 4.4$ Hz to approximate the outer peak separation, the proton decoupled ^{13}C spectra of these compounds were simulated by the ITRCAL[1] program. This result simply supports the reasonableness of the assumption that $^3J^{31}P^{13}C$ is very small in these compounds.

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