density between the atoms. This density, however, along a P–P line is far from symmetric side to side, as expected for bent bonds. The $4a_1$ MO is the electron density complement of $5a_1$, being bonding along the P–P line, with a low density behind the vertices and a high density *within* the triangular face. Thus, as with cyclopropane, the various MO's are bent both outward and inward. The strong antibonding character of the $5t_2$ MO is evident as a trough at midpoint. It is hoped that these contours might be of future value in understanding the chemistry of the P_4 molecule, for example, in elucidating the recently discovered bonding of molecular P_4 in various rhodium complexes.[23]

Acknowledgment.—It is a pleasure to acknowledge the contribution of Miss Mary Dolan, who calculated the electron densities.

[23] A. P. Ginsberg and W. E. Lindsell, *J. Amer. Chem. Soc.*, **93**, 2082 (1971).

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A Nuclear Magnetic Resonance Investigation of the Bonding in Fourth-Group Phenylphosphines[1]

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The compounds $(CH_3)_3MPHC_6H_5$ where M = C, Si, and Sn have been synthesized, and $J(^{31}P-^{1}H)$ values recorded. Infrared assignments in the region 4000–400 cm^{-1} are also presented. Controlled oxidation of the tin compound yields $(CH_3)_3SnOPHC_6H_5$ as established by ^{31}P couplings which also give information concerning the exchange of groups at phosphorus in mixtures of the two tin compounds. The one-bond $^{31}P-^{1}H$ couplings have been interpreted in terms of a pyramidal arrangement of bonds at phosphorus.

We have been engaged for some time in investigations designed to test the hypothesis of $(p \rightarrow d)\pi$ contributions to the bonds formed between nitrogen and the fourth-group elements silicon, germanium, and tin. We have reported the results of nmr studies on derivatives of aniline-^{15}N containing these elements where $J(^{15}N-^{1}H)$ values were measured and interpreted in terms of the stereochemistry and bonding at nitrogen.[2,3] In this paper we extend the treatment to phosphorus.

Experimental Section

Apparatus.—The nmr data were obtained on a Varian HA-100D spectrometer using a benzene lock in the frequency sweep mode. Infrared spectra were recorded as liquid films on a Beckman IR-12 instrument and calibrated with polystyrene.

Syntheses.—All manipulations were carried out under an inert atmosphere of nitrogen or argon in a Vacuum Atmospheres Corp. glove box equipped with a Model HE-193-1 Dri-Train. Boiling points are uncorrected.

***tert*-Butylphenylphosphine (I).**—Phenyldichlorophosphine (0.05 mol) in methylene chloride (4 ml) was added with stirring during 45 min to freshly sublimed aluminum chloride (6.7 g, 0.05 mol) in methylene chloride (10 ml). After a further 45 min the solution was cooled to 10° and *tert*-butyl chloride (5.8 g, 0.062 mol) was added during 1 hr. The solution was then added to chloroform (25 ml) and poured into concentrated hydrochloric acid (16 ml) and crushed ice (50 g). The aqueous layer was separated and extracted with chloroform (two 5-ml portions) and the solvent was removed under reduced pressure from the combined organic layer. The crude *tert*-butylphenylphosphinic chloride was not purified further but was reduced using lithium aluminum hydride in ether to *tert*-butylphenylphosphine (bp 110–113° (16 mm); 5.95 g, 72% yield). *Anal.* Calcd for $C_{10}H_{15}P$: C, 72.27; H, 9.05. Found: C, 71.41; H, 8.77.

Trimethylsilylphenylphosphine (II).—*n*-Butyllithium (31.3 ml, 1.6 *M* in hexane, 0.05 mol) was added dropwise with stirring to phenylphosphine (5.5 g, 0.05 mol) in ether (50 ml) to form the pale yellow monolithiophosphine. Trimethylchlorosilane (5.5 g, 0.05 mol) in ether (20 ml) was added dropwise. The yellow color was discharged, and lithium chloride precipitated and was filtered. Solvents were then removed under reduced pressure, and the residue was distilled trap to trap (room temperature to 77°K at 0.1 mm) to yield trimethylsilylphenylphosphine as a mobile, colorless liquid (4.1 g, 45%). *Anal.* Calcd for $C_9H_{15}PSi$: Si, 15.8. Found: Si, 15.2. The product is very sensitive to atmospheric moisture and oxygen.

Trimethylgermylphenylphosphine (III) was prepared according to the published method.[4]

Trimethylstannylphenylphosphine (IV).—*n*-Butyllithium (31.3 ml, 1.6 *M* in hexane, 0.05 mol) was added dropwise with stirring to phenylphosphine (5.5 g, 0.05 mol) in dry ether (50 ml) to form the monolithiophosphine. Trimethyltin chloride (10 g, 0.05 mol) in tetrahydrofuran (30 ml) was added over 0.5 hr with stirring. The yellow color of the lithiophosphine was discharged, and lithium chloride precipitated and was filtered. The solvent was removed under reduced pressure and the residue was carefully distilled to yield trimethylstannylphenylphosphine as a very moisture- and oxygen-sensitive, mobile, colorless liquid (bp 38° (0.1 mm); 3.1 g, 22.7%). *Anal.* Calcd for $C_9H_{15}PSn$: C, 39.6; H, 5.5; Sn, 43.5. Found: C, 38.9; H, 5.1; Sn, 43.0.

Trimethylstannoxyphenylphosphine (V) was made by controlled oxidation of IV in the drybox.

Results and Discussion

The carbon, silicon, and tin derivatives of phenylphosphine are new compounds. The *tert*-butyl group was attached to phosphorus by the method of Crofts and Parker[5] as shown in eq 1. The reaction of *tert*-butyl chloride with the monolithium derivative of phenylphosphine yields mainly *sec*-butane,

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[1] A preliminary account of this work has appeared: P. G. Harrison, S. E. Ulrich, and J. J. Zuckerman, *J. Amer. Chem. Soc.*, **93**, 2307 (1971).

[2] (a) E. W. Randall, J. J. Ellner, and J. J. Zuckerman, *J. Amer. Chem. Soc.*, **88**, 622 (1966); (b) E. W. Randall and J. J. Zuckerman, *ibid.*, **90**, 3167 (1968).

[3] E. W. Randall and J. J. Zuckerman, *Chem. Commun.*, 732 (1966).

[4] I. Schumann-Ruidisch and J. Kuhlmey, *J. Organometal. Chem.*, **16**, P26 (1969).

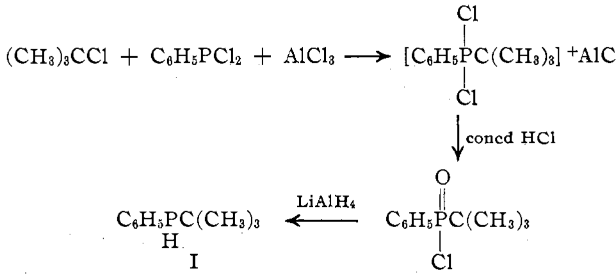
[5] P. C. Crofts and D. M. Parker, *J. Chem. Soc. C*, 332 (1970).

TABLE I

NMR PARAMETERS OF PHENYLPHOSPHINES (Hz)[a]

	$\delta(CH_3)$[b]	$\delta(PH)$[b]	$J(^{31}P–M–C–^1H_3)$	$J(^{31}P–^1H)$
$C_6H_5PH_2$	. . .		. . .	205.5[c]
$C_6H_5PHC(CH_3)_3$ (I)	124.7 ± 0.5	405.5 ± 0.5	12.4 ± 0.1	205.7 ± 0.5
$C_6H_5PHSi(CH_3)_3$ (II)	45.8 ± 0.5	404.2 ± 0.5	4.4 ± 0.1	200.6 ± 0.5
$C_6H_5PHGe(CH_3)_3$ (III)	28.3[d,e]	323.8[d,f]	3.5[d]	194.5[d]
$C_6H_5PHSn(CH_3)_3$ (IV)	45.3 ± 0.5	378.5 ± 0.5	1.9 ± 0.2	187.1 ± 0.5
$C_6H_5PHOSn(CH_3)_3$ (V)	57.1 ± 0.5	419.0 ± 0.5	2.0 ± 0.1[g]	197.4 ± 0.5

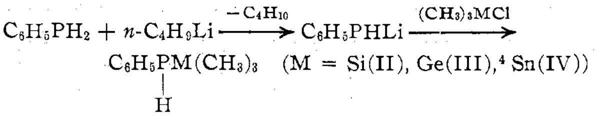
[a] Recorded on 20% solutions in benzene using a Varian HA-100D spectrometer. [b] Proton chemical shifts are listed *vs.* tetramethylsilane at 100 MHz. [c] Reference 9. [d] Reference 4. [e] Reported as 17.0 Hz *vs.* tetramethylsilane at 60 MHz. [f] Reported as 194.3 Hz *vs.* tetramethylsilane at 60 MHz. [g] $J(^{31}P–O–Sn–C–^1H)$.



$$(CH_3)_3CCl + C_6H_5PCl_2 + AlCl_3 \longrightarrow [C_6H_5\overset{Cl}{\underset{Cl}{P}}C(CH_3)_3]^+AlCl_4^- \quad (1)$$

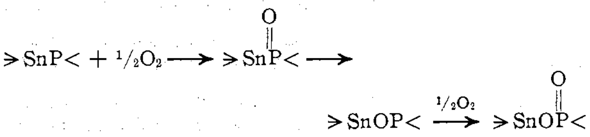
$$\xrightarrow{\text{concd HCl}} C_6H_5\overset{O}{\underset{Cl}{P}}C(CH_3)_3 \xrightarrow{LiAlH_4} \underset{\text{I}}{C_6H_5\underset{H}{P}C(CH_3)_3}$$

but with the lower fourth-group chlorides the substituted phenylphosphine is obtained[6]



$$C_6H_5PH_2 + n\text{-}C_4H_9Li \xrightarrow{-C_4H_{10}} C_6H_5PHLi \xrightarrow{(CH_3)_3MCl} C_6H_5\underset{H}{P}M(CH_3)_3 \quad (M = Si(II), Ge(III),^4 Sn(IV)) \quad (2)$$

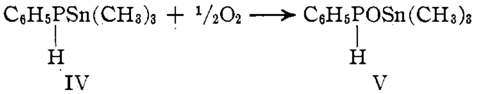
The products are mobile liquids with the organometallic compounds very susceptible to hydrolysis and air oxidation. The tin derivative is particularly easily oxidized, and according to previous work on tin–phosphorus compounds the following mechanism was proposed



$$>SnP< + {}^1/_2O_2 \longrightarrow >Sn\overset{O}{P}< \longrightarrow >SnOP< \xrightarrow{{}^1/_2O_2} >SnO\overset{O}{P}< \quad (3)$$

where the addition of oxygen to the phosphorus lone pair is the initial step, followed by rearrangement to the tin–oxygen–phosphorus compound.[7] Oxidation of the related triphenylstannyldiphenylphosphine proceeds directly to the final phosphine oxide product containing two oxygen atoms. The >SnOP< intermediate could not be isolated from the air-exposed mixture, but was prepared separately and shown to undergo ready oxidation to >SnOP(=O)<. Synthetic routes designed to yield the >SnP(=O)< system give only the rearranged >SnOP< product.[7,8]

We have allowed our tin derivative (IV) to undergo controlled oxidation in a glove box and have measured the nmr parameters of the product. The values of $J(^{31}P–^1H)$ as shown in Table I specify the oxidation as[9]



$$\underset{\text{IV}}{C_6H_5\underset{H}{P}Sn(CH_3)_3} + {}^1/_2O_2 \longrightarrow \underset{\text{V}}{C_6H_5\underset{H}{P}OSn(CH_3)_3} \quad (4)$$

to give the phosphorus(III) compound as the only observed product. The values of $J(^{31}P–^1H)$ for structures of the type >P(O)H are in the range 490–760 Hz.[9] If the reaction does in fact proceed through an initial addition of oxygen to the phosphorus atom, then this must be the rate-controlling step in the formation of V, and the subsequent rearrangement must be rapid with respect to the nmr time scale.

Further controlled oxidation leads to slow precipitation of what is likely to be the pentavalent phosphonate system, >SnO(O)P<. The analogous triphenylstannyldiphenylphosphonate is also insoluble. We have prepared trimethylstannyldiphenylphosphine[10] and found it much less sensitive to oxidation than its monophenyl analog.

The four-bond coupling $J(^{31}P–O–Sn–C–^1H)$ is the first such reported. We can offer no explanation for its equivalent magnitude with the three-bond coupling, $J(^{31}P–Sn–C–^1H)$. The observation of separate resonances for the methyl portions of the spectra of IV and V in a mixture of the two compounds produced by partial oxidation of IV at ambient temperatures, as well as observation of the coupling $J(^{31}P–Sn–C–^1H)$ and $J(^{31}P–O–Sn–C–^1H)$ and the much larger couplings $J(^{31}P–^{119}Sn)$[11] and $J(^{31}P–O–^{119}Sn)$,[11] rules out exchange phenomena involving breakage of the tin–phosphorus bond which is rapid with respect to the nmr time scale [in excess of $2\pi \times 1.9$ sec^{-1} or 12 sec^{-1}, taking the smallest of the couplings ($J(^{31}P–Sn–C–^1H)$) observed]. However, spectra recorded at 125° show the coalescence of the two methyl resonances and the disappearance of the couplings $J(^{31}P–Sn–C–^1H)$ and $J(^{31}P–O–Sn–C–^1H)$. Two $J(^{31}P–^1H)$ couplings are seen even at 150°, ruling out rapid exchange processes involving that bond. The spectral changes are reversible with temperature, and similar phenomena have been studied for tin amines.[12]

Infrared Spectra.—The infrared absorptions for the three compounds $(CH_3)_3MPHC_6H_5$ where M = C, Si, and Sn are listed in Table II, with assignments derived from those for phenylphosphine itself by comparison.[13,14] It is likely that the M–P stretching fre-

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[6] An excellent review of organo group IV phosphines has recently appeared: E. W. Abel and S. M. Illingworth, *Organometal. Chem. Rev., Sect. A*, **5**, 143 (1970).

[7] H. Schumann, P. Jutzi, A. Roth, P. Schwabe, and E. Schauer, *J. Organometal. Chem.*, **10**, 71 (1967).

[8] K. Issleib and B. Walther, *Angew. Chem.*, **79**, 449 (1967).

[9] G. Mavel in "Progress in Nmr Spectroscopy," J. W. Emsley, J. Feeney, and L. H. Sutcliffe, Ed., Vol. 1, Pergamon Press, Oxford, 1965, p 251; M. M. Crutchfield, C. H. Dungan, J. H. Letcher, V. Mark, and J. W. Van Wazer, "P³¹ Nuclear Magnetic Resonance," Interscience, New York, N. Y., 1967; J. M. Van Wazer in "Determination of Organic Structures by Physical Methods," F. C. Nachod and J. J. Zuckerman, Ed., Vol. 4, Academic Press, New York, N. Y., 1971, p 207.

[10] G. M. Campbell, G. W. A. Fowles, and L. A. Nixon, *J. Chem. Soc.*, 1389 (1964); K. Jones and M. F. Lappert, *Proc. Chem. Soc., London*, 22 (1964).

[11] P. G. Harrison, S. E. Ulrich, and J. J. Zuckerman, *Inorg. Nucl. Chem. Lett.*, **7**, 865 (1971).

[12] E. W. Randall, C. H. Yoder, and J. J. Zuckerman, *J. Amer. Chem. Soc.*, **89**, 3438 (1967).

[13] R. L. Amster and N. B. Colthup, *Spectrochim. Acta*, **19**, 1849 (1953).

[14] J. Goubeau and D. Langhardt, *Z. Anorg. Allg. Chem.*, **338**, 163 (1965).

TABLE II: THE INFRARED SPECTRA (4000–500 CM^{-1}) OF $C_6H_5PHM(CH_3)_3$ WHERE M = C, Si, AND Sn[a]

$(CH_3)_3CP(H)C_6H_5$	$(CH_3)_3SiP(H)C_6H_5$	$(CH_3)_3SnP(H)C_6H_5$	Assignment
		3148 vw	ν(C–H) and ν(C–C) combinations
3075 m	3070 m	3075 m	
3060 m	3058 m	3065 m, sh	
3030 m, sh			
3020 m	3020 w		
3005 m		3010 m	
2955 vs	2955 m	2970 m	
2938 vs	2925 m	2925 m	
2895 vs	2870 s	2880 w, sh	
2862 vs	2855 m		
2825 w, sh			
2810 vs, sh			
2780 vw, sh		2790 vs	
2745 vw			
2715 vw			
2365 w, sh	2370 m, sh	2365 m, sh	
2340 w, sh			
2288 s	2290 s	2295 vs	ν(P–H)[b]
		2140 vw, sh	Combination bands
		1971 vw, sh	
1955 vw	1947 vs	1955 vs	
1895 vw	1895 vw	1900 vw	
1883 vw		1890 vw	
1817 vw	1810 vw	1815 vw	
1779 vw			
1762 vw		1745 vw	
		1710 vw	
1660 vw		1643 vw	
1591 vw	1592 w	1592 vw	ν(C–C)
1573 vw	1575 w	1580 w	
1550 vw			
1482 s	1481 m	1483 s	
1461 s	1461 w	1462 w	
1436 s	1435 s	1438 vs	
1415 w		1405 w, br	
1392 w			
1365 s	1380 vw		
1329 w	1331 vw	1332 w	
1310 w	1297 vw	1300 w	δ(C–H)
1282 w, sh			
1264 w	1253 s	1256 vw	
1214 vw, sh			
1189 m		1195 m	
1161 m		1178 w, br	
1128 m	1126 m	1125 w, sh	
1103 m	1109 s	1111 m	ν(C–P)
1072 m	1070 vs	1077 s	β(C–H)
1029 s	1027 s	1029 m	β(C–H)
1021 m, sh			Phenyl ring deformations
1005 w, sh	1002 m	1002 w	
989 w, sh		990 w, sh	
973 w, sh	977 m		
941 w			β(C–H)
919 w	927 w	915 w, sh	
889 m	885 w, sh	875 w, sh	
		850 m, sh	
	846 vs		Si–CH$_3$ rock
821 m	826 s	826 s	β(C–H)
791 m			
		786 vs	Sn–CH$_3$ rock
	756 m		β(C–H)
	751 m, sh		
743 vs	720 vs	727 vs	
701 vs	692 s	696 s	$(\mathrm{SiC}_3)_{\mathrm{asym}}$, δ(C–P)
676 vw, sh	675 w, sh	680 w, sh	β(C–H)
650 vw, sh		652 vw, sh	
	649 vw		$\nu(\mathrm{SiC}_3)_{\mathrm{sym}}$
620 vs	622 vs	623 vs	α(C–C–C)
586 w			
560 vw			
		547 vs	$\nu(\mathrm{SnC}_3)_{\mathrm{asym}}$
536 vw	535 w		
		522 m	$\nu(\mathrm{SnC}_3)_{\mathrm{sym}}$
523 vw	522 w		
500 m			

[a] Recorded as liquid smears. [b] Reported at 2290 cm^{-1} (s) in $(CH_3)_3GePHC_6H_5$.[4]

quencies where M = Si and Sn lie below 500 cm^{-1}. The ν(Sn–P) mode in $(C_6H_5)_3SnP(C_6H_5)_2$ has been assigned to a medium-intensity band at 351 cm^{-1}[7] and the ν(Ge–P) mode in $(CH_3)_3GePHC_6H_5$ to a strong absorption at 354 cm^{-1}.[6] It is noteworthy that although there is a large change (−80 cm^{-1}) in the ν(P–H) absorption between phosphine and phenylphosphine,[14] the effect of the substitution of $M(CH_3)_3$ for hydrogen where M = C, Si, Ge[4], or Sn is negligible. The absorption assigned to ν(C–P) is likewise insensitive to the substitution by $M(CH_3)_3$, although large changes are seen on halo substitution at phosphorus.[14]

Nmr.—The suggestion that the magnitude of the one-bond ^{15}N–^1H coupling can be correlated with the stereochemical situation at nitrogen and hence with nitrogen bond hybridization has been tested with reference to a large number of nitrogenous compounds with good result.[15,16] The data serve to establish a scale of hertz values which range from the low seventies for tetrahedral nitrogen as in NH_4^+ (73.2[15] or 73.7[17] Hz) to approximately 100 Hz for trigonal-planar nitrogen as in the pyridinium ion (90.5[15] or 98.7[16] Hz) or pyrrole (*ca.* 100 Hz).[18] Values for various amides lie between 88.0 and 92.6 Hz.[16] The progression of values suggests that the Fermi-contact interaction is dominant and that the coupling is proportional to the square of the coefficient of the N(2s) wave function in the LCAO treatment of the nitrogen hybrid orbital in the sequence sp^3, sp^2, sp. Examples of the last type, RC≡NH, have coupling constants of 130–136 Hz.[19] By contrast the negligible effect on $J(^{15}N\text{–}^1H)$ in the presumably already sp^2-hybridized anilinium, indolinium, and quinolinium ions on nitro substitution[20] serves to rule out substituent, inductive, or field effects as controlling the magnitude of the coupling through the mean triplet excitation energy term in the Fermi-contact mechanism.

The magnitude of $J(^{15}N\text{–}^1H)$ for aniline-^{15}N (78–81 Hz)[2a,3,21,22] reveals conjugation between the nitrogen lone pair and the phenyl group, but the value is considerably lower than that associated with planar nitrogen (sp^2). This result for aniline has found confirmation in microwave work which establishes the nonplanarity with ∠HNH = 113° 16′.[23] Conjugation with the phenyl ring can be enhanced by substitution of groups such as *p*-NO$_2$ (88.9[21] or 89.2[22] Hz), *p*-Cl (83.7[22] Hz), *p*-Br (83.6[21] or 84.0[22] Hz), and *p*-I (84.1[21] or 84.0[22] Hz) which serve to increase the coupling constant, while *p*-F (81.6 Hz[22]) and *p*-OCH$_3$ (79.4 Hz[22]) decrease the value as does conversion to the anilinium ion (75.0[21] or 76.0[20] Hz). A recent microwave study confirms that *p*-fluoroaniline is farther from planarity than aniline itself (∠HNH = 111°

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(15) G. Binsch, J. B. Lambert, B. W. Roberts, and J. D. Roberts, *J. Amer. Chem. Soc.*, **86**, 5564 (1964).

(16) A. J. R. Bourn and E. W. Randall, *Mol. Phys.*, **8**, 567 (1964).

(17) J. D. Baldeschwieler, *J. Chem. Phys.*, **36**, 152 (1962).

(18) J. D. Roberts, private communication quoted in ref 2b.

(19) G. A. Olah and T. E. Kiovsky, *J. Amer. Chem. Soc.*, **90**, 4555 (1968); G. A. Olah and A. M. White, *ibid.*, **90**, 6088 (1968); H. Hogeveen, *Recl. Trav. Chim. Pays-Bas*, **86**, 1288 (1967).

(20) T. Axenrod, M. J. Wieder, G. Berti, and P. J. Barilli, *J. Amer. Chem. Soc.*, **92**, 6066 (1970).

(21) M. R. Bramwell and E. W. Randall, *Chem. Commun.*, 250 (1969).

(22) T. Axenrod, P. S. Pregosin, M. J. Wieder, and G. W. A. Milne, *J. Amer. Chem. Soc.*, **91**, 3681 (1969).

(23) D. G. Lister and J. K. Tyler, *Chem. Commun.*, 152 (1966).

52′).[24] N-Substitution in aniline by groups capable of conjugation, such as those containing α unsaturation, leads to an increase in $J(^{15}N{-}^{1}H)$ to 89.7–96.1 Hz.[25] N-Substitution of groups such as the silyl, germyl, or stannyl, capable of d-orbital conjugation with the nitrogen lone pair, however, results in the lowering of $J(^{15}N{-}^{1}H)$ (to 76.0, 77.1, 73.8 Hz, respectively) below that found in aniline itself, and replacing the phenyl ring by a second trimethylsilyl group lowers the value still further (66.5 Hz).[2b,26] Adjacent atoms capable of d-orbital conjugation can, when substituted by strongly electronegative groups, effect substantial increases in $J(^{15}N{-}^{1}H)$ as in the aminophosphine $(CF_3)_2PNH_2$ (85.6 Hz), the phosphorane $F_3P(NH_2)_2$ (87.5 Hz), and the sulfenamide $(CF_3S)_2NH$ (99.1 Hz) where the values reflect a nitrogen atom hybridization close to sp^2.[27] Structural studies reveal that the nitrogen atom is planar in the related aminophosphines $F_2PN(CH_3)_2$ (X-ray)[28] and F_2PNH_2 (microwave).[29] The J values for these compounds should be compared with those of compounds where the adjacent phosphorus atom is less strongly substituted by electronegative groups, as in $CF_3(CH_3)PNH_2$ (78.9 Hz) and $[CF_3(CH_3)P]_2NH$ (77.4 and 78.9 Hz for the two phosphorus chiral centers), where only a single CF_3S group is attached as in CF_3SNH_2 (80.6 Hz), or where the adjacent atom is arsenic as in $(CF_3)_2AsNH_2$ (76 Hz) and $[(CF_3)_2As]_2NH$ (79.0 Hz) which reflect a hybridization at nitrogen closer to sp^3.[27] It should be noted that while in the perfluoromethylsulfur and -arsenic compounds disubstitution raises the value of $J(^{15}N{-}^{1}H)$,[27] the opposite effect is observed in the methylsilylamines,[2b] and little change in J accompanies substitution of a second $CF_3(CH_3)P$ group.[27]

The situation with respect to the one-bond $^{31}P{-}^{1}H$ coupling constants is similar. Substitution of conjugating groups on phosphorus increases $J(^{31}P{-}^{1}H)$. For example, while successive methyl substitution of PH_3 raises the magnitude of the coupling from 183[30] to 187.8[31] and 191.0[31] Hz ($\sim$2% per methyl group), phenyl substitution (see Table I) gives rise to a larger increase (13%), and substitution of phenylphosphine by a second phenyl group raises this value still further (to 214 Hz),[32] while alkyl substitution, on the other hand, introduces hardly any change at all. No structural data are available for the phenylphosphines, but Raman and infrared studies suggest phenylphosphine to be nonplanar, possessing C_s symmetry.[13]

Thus as is the case with $J(^{15}N{-}^{1}H)$ values discussed above, the substitution of groups capable of involving the phosphorus lone pair raises the magnitude of the coupling. Then substitution of silicon, germanium, or tin for hydrogen in phenylphosphine should raise the $J(^{31}P{-}^{1}H)$ value if $(p \rightarrow d)\pi$ conjugation is important. We find instead as is seen in Table I that the organometallic phenylphosphines exhibit lower values than either *tert*-butylphenylphosphine or phenylphosphine itself. Substitution of a second group capable of d-orbital conjugation, as in $[(CH_3)_3Si]_2PH$, lowers the value still further (to 186 Hz).[33] The $J(^{31}P{-}^{1}H)$ values in $(CH_3)_3MPH_2$ [(M = Si (180 Hz)[33] and Sn (169.5 Hz)[34]] are also lower than the value in phosphine itself (183 Hz).[30]

The $(p \rightarrow d)\pi$ bonding hypothesis is thus not necessary to explain these data which change in a way opposite to that expected from π conjugation with phosphorus. The earlier proposal of a planar structure for $(H_3Si)_3P$ made on the basis of vibrational spectroscopy has now been revised by electron diffraction studies which confirm the pyramidal nature of the heavy-atom skeleton with $\angle SiPSi = 95°$.[35] Furthermore, vibrational spectroscopic data indicate that $(p \rightarrow d)\pi$ interactions are not stereochemically significant in trigermylphosphine[36] or in $[(CH_3)_3Sn]_3P$,[37] and the force constants of the Si–P system are consistent with single-bond character.[38] The rather low barriers to inversion at phosphorus recently estimated by nmr techniques in trimethylsilyl- and trimethylgermyl-substituted phenylisopropylphosphines ($\Delta G^{\ddagger}_{62}$ = 18.9 and $\Delta G^{\ddagger}_{109}$ = 21.4 kcal/mol, respectively), initially interpreted in terms of enhanced $(p \rightarrow d)\pi$ interaction in the transition state for inversion,[39] have now been reinterpreted with the trimethylstannyl derivative ($\Delta G^{\ddagger}_{72}$ = 19.3 kcal/mol) on the basis of a ligand electronegativity effect.[40] Our nmr results on the ground states, as in the case of the analogous amines,[2,3,41] are adequately dealt with by considering redistributions of electrons in the σ framework of the molecules only.

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(24) A. Hastie, D. G. Lister, R. L. McNeil, and J. K. Tyler, *Chem. Commun.*, 108 (1970).

(25) A. J. R. Bourn, D. G. Gillies, and E. W. Randall, *Tetrahedron*, **20**, 1811 (1964); A. K. Bose and I. Kugajevsky, *ibid.*, **23**, 1489 (1967).

(26) The $J(^{15}N{-}^{1}H)$ in $(H_3Si)_2NH$ has been recently measured to be 71.4 Hz: A. J. Cowley, private communication, 1971.

(27) A. H. Cowley and J. R. Schweiger, *Chem. Commun.*, 1492 (1970); A. H. Cowley, M. J. S. Dewar, W. R. Jackson, and W. B. Jennings, *J. Amer. Chem. Soc.*, **92**, 5206 (1970).

(28) E. D. Morris and C. E. Nordman, *Inorg. Chem.*, **8**, 1672 (1969).

(29) A. H. Brittain, J. E. Smith, and R. H. Schwendeman, unpublished results quoted by J. E. Smith, R. Steen, and K. Cohn, *J. Amer. Chem. Soc.*, **92**, 6359 (1970).

(30) R. M. Lynden-Bell, *Trans. Faraday Soc.*, **57**, 888 (1961).

(31) S. L. Manatt, G. L. Juvinall, R. L. Wagner, and D. D. Elleman, *J. Amer. Chem. Soc.*, **88**, 2689 (1966).

(32) K. Moedritzer, L. Maier, and L. C. D. Groenweghe, *J. Chem. Eng. Data*, **7**, 307 (1962).

(33) E. Fluck, H. Burger, and U. Goetze, *Z. Naturforsch. B.*, **22**, 912 (1967).

(34) A. D. Norman, *J. Organometal. Chem.*, **28**, 81 (1971).

(35) B. Beagley, A. G. Robiette, and G. M. Sheldrick, *Chem. Commun.*, 601 (1967); *J. Chem. Soc. A*, 3002 (1968).

(36) S. Cradock, G. Davidson, E. A. V. Ebsworth, and L. A. Woodward, *Chem. Commun.*, 515 (1965).

(37) R. E. Hester and K. Jones, *ibid.*, 317 (1966).

(38) G. Davidson, E. A. V. Ebsworth, G. M. Sheldrick, and L. A. Woodward, *Spectrochim. Acta*, **22**, 57 (1966).

(39) R. D. Baechler and K. Mislow, *J. Amer. Chem. Soc.*, **92**, 4758 (1970).

(40) R. D. Baechler and K. Mislow, *ibid.*, **93**, 773 (1971).

(41) ^{15}N generally resembles ^{31}P in its pattern of coupling constants; the ^{15}N nucleus has a negative magnetogyric ratio, and the reduced coupling constant $K(^{15}N{-}^{1}H)$ in $(CF_3)_2PNH_2$ has a relative positive sign: A. H. Cowley, J. R. Schweiger, and S. L. Manatt, *Chem. Commun.*, 1491 (1970). It has been proposed that $J(^{31}P{-}^{1}H)$ can be considered as having an absolute positive sign,[31] and this assumption leads to reasonable relative signs in IV and $(CH_3)_3SnP(C_6H_5)_2$.[11]