tion of the phenyl substituent, a linear relationship exists for the para and meta series. The ortho series suffers from (a) anisotropic effects of the substituents on the δ and (b) uncertainty in the values of σ_o[10] chosen. The δ values were found to be quite solvent dependent (in methylene chloride), with the compounds having the more polar substituents generally being the most affected.

The large solvent effect makes any comparison of the ρ values for phenylsilanes with those of *tert*-butylbenzenes, dimethylanilines, and anisoles questionable. However, the ρ values for **2** are similar to those for **3** ($(Si(CH_3)_3)_m$, 6.86 cps/σ; $(Si(CH_3)_3)_p$, 3.99 cps/σ; $C(CH_3)_3$, 4.56 cps/σ), while those for **4** (9.59 cps/σ) and **5** (16.2 cps/σ) are greater, owing probably to the presence of lone electron pairs in the latter two.[4] Such correlations of δ and σ for protons are common,[5] but the magnitude of the effect is generally small and the system is not sensitive to small changes in the electron distribution. The similarity between the ρ values of *tert*-butylbenzenes and phenyltrimethylsilanes has been reported (5.38 *vs.* 5.86 cps/σ, measured at 60 MHz).[1m]

In conclusion, the correlation of *J vs.* σ in substituted phenyltrimethylsilanes indicates that silicon's effective electronegativity is more affected by the nature of the substituent than that for the analogous atom in comparable carbon, nitrogen, and oxygen compounds. This is particularly pronounced when the silicon is para, permitting the maximum effect of $(p \rightarrow d)\pi$ back-bonding between the phenyl π system and the silicon 3d orbitals. When the π-electron density of the phenyl is significantly reduced, as with the strong electron-acceptor substituents $-CF_3$ and $-NO_2$, the *J* values do not correlate with σ for the ortho and para isomers. The correlation of *J vs.* σ over the entire range of meta substituents suggests that the degree of $(p \rightarrow d)\pi$ back-bonding here is smaller than that in the directly conjugated ortho and para cases. The same trend of para substitution being more effective than meta substitution for transmission of the electronic effects is observed in the correlation of δ *vs.* σ.

The magnitude of the shifts are quite small, suggesting either that $(p \rightarrow d)\pi$ back-bonding in the ground state is not a large effect or that the $^{13}C-H$ coupling constants are not a sensitive test of this effect. Work is currently in progress to determine the $^{29}Si-^1H$ coupling constants of the series $X-C_6H_4-SiH_3$ to resolve this point. Additionally, because of the reduced number of basis sets required for $-SiH_3$ (relative to $-SiMe_3$), MO calculations will allow a differentiation between polarization effects and $(p \rightarrow d)\pi$ back-bonding. These problems will be dealt with in a later paper.

Acknowledgment. The authors wish to thank the Department of Chemistry, University of Iowa, Iowa City, Iowa, for making the HA-100 available to M.E.F., and Mr. Douglas C. Kirk, for technical assistance.

The Phosphorus–Phosphorus Bond. I. Complexes Containing Highly Connected Phosphorus Atoms, $H_nMe_{3-n}PPF_5$. The Directly Bonded Phosphorus–Phosphorus Coupling Constant

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Abstract: The reaction of alkylphosphines with PF_5 has produced the Lewis adducts $Me_3P \rightarrow PF_5$, $HMe_2P \rightarrow PF_5$, and $H_2MeP \rightarrow PF_5$, which have been characterized by nmr spectroscopy and reaction stoichiometry. These molecules ostensibly contain both octahedral and tetrahedral P-atom environments. The trimethylphosphine complex is a white solid which is stable at 25° *in vacuo*, but there is a marked decrease in stability as the number of hydrogen atoms in the molecule is increased. Equilibrium studies showed that the complexes have a stronger P–P coordinate bond than the similar P–N bond and that PF_5 is a stronger acid than BF_3 toward PMe_3. Although $^2J_{PF_{eq}}$ approximates +200 Hz for all three adducts, $^2J_{PF_{ax}}$ is zero. The P–P coupling in these molecules (+720 Hz) is the largest ever observed for a direct P–P bond. Evidence is presented which favors the dominance of the orbital and/or dipolar contributions to $^1J_{PP}$ when at least one phosphorus has a lone pair of electrons.

The facility of complex formation between PF_5 and donor molecules such as amines and ethers[1,2] and a brief report of Me_3PPF_5[3] led us to treat phosphorus pentafluoride with alkylphosphines in order to test the viability of a P–P bond constituted by P atoms of high connectivity. The envisaged $H_nR_{3-n}P_P \rightarrow PF_5$ coordinate link affords a "model" single bond since neither of the P atoms possesses a lone pair of electrons which might enter into p_π–d_π multiple bonding.[4] The sign and magnitude of $^1J_{PP}$ for a model single bond is of particular interest since only one other such sign de-

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(1) E. L. Muetterties, T. A. Bither, F. W. Farlow, and D. D Coffman, *J. Inorg. Nucl. Chem.*, 16, 52 (1960).

(2) F. N. Tebbe and E. L. Muetterties, *Inorg. Chem.*, 6, 129 (1967).

(3) D. H. Brown, K. D. Crosbie, G. W. Fraser, and D. W. A. Sharp, *J. Chem. Soc. A*, 551 (1969).

(4) A. H. Cowley, *Chem. Rev.*, 65, 617 (1965).

Table I. Nmr Data

Bond relationship between coupled nuclei	Chemical[a] shift	J[b]	Me_3PPF_5[c]	Me_2HPPF_5[d]	MeH_2PPF_5[e]
^{19}F Nmr Data					
F_{eq}–P_α		$^1J_{PF_{eq}}$	−900	−873	−867
F_{eq}–P–P_β		$^2J_{PF_{eq}}$	+183	+184	+220
F_{eq}–P–F_{ax}		$^2J_{F_{eq}F_{ax}}$	−51.5, −52[f]	−53.6, −52.8[f]	−59, −59[f]
F_{eq}–P–P–H		$^3J_{HF_{eq}}$		6.5	7.7
F_{ax}–P_α		$^1J_{PF_{ax}}$	−784	−783	−800
	$\delta(F_{eq})$		+51.3	+44.7	+37.1
	$\delta(F_{ax})$		+77.3	+78.7	+80.0
^{1}H Nmr Data					
P_β–H		$^1J_{PH}$		425	g
P_α–P–H		$^2J_{PH}$		24.5, 31.0[h]	g
H–P–C–H		$^3J_{HH}$		6.5, 6.5[f]	7.0
H–P–P–F_{eq}		$^3J_{HF_{eq}}$		g	6.5
H–C–P_β		$^3J_{PH}$	13.5	15.7	17
H–C–P–P_α		$^3J_{PH}$	9.5	10.9	11
H–C–P–P–F_{eq}		$^4J_{HF_{eq}}$	1.1	0.5	g
	δ(H)			+0.81	g
	$\delta(CH_3)$		+0.35	+2.64	+0.13
^{31}P Nmr Data					
P–P		$^1J_{PP}$	+715, 720	+714, 723	g
P–H		$^1J_{PH}$		416	g
P_α–F_{eq}		$^1J_{PF_{eq}}$	−890	−887	g
P_α–F_{ax}		$^1J_{PF_{ax}}$	−780	−780	g
P_β–P–F_{eq}		$^2J_{PF_{eq}}$	+175	+202	g
P_β–C–H		$^2J_{PH}$	g	15.4	g
	$\delta(P_\alpha)$		+120	+149	g
	$\delta(P_\beta)$		−24	−11	g

[a] Chemical shift values are given in parts per million from $CFCl_3$ (^{19}F spectra) and H_3PO_4 (^{31}P spectra), and were obtained by tube interchange except in the case of the pmr data, which are reported relative to the position of the solvent resonance. [b] Given in hertz. The signs which are noted were determined for Me_3PPF_5 and should be the same in the other complexes. [c] Spectra were obtained at −37° in CH_3CN. [d] Spectra were obtained at −10° in CH_2Cl_2. [e] Spectra were obtained at −75° in CH_3Cl. [f] Two separate values were obtained from the appropriate regions of the spectrum. [g] Could not be observed because of the weak signal. [h] The correct value is probably 24.5, but owing to the weak signal the extent of overlap in the multiplet was not clearly evident.

termination is reported,[5] the latter being the only positive $^1J_{PP}$.[5b]

The new complexes are analogous to the known compounds $Me_3N \rightarrow PF_5$,[1] $HMe_2N \rightarrow PF_5$,[6] and $H_2MeN \rightarrow PF_5$.[7]

Results and Discussion

Characterization. Treatment of phosphorus pentafluoride with methyl-, dimethyl-, and trimethylphosphine gives 1:1 complexes which are readily characterized by nmr spectroscopy as neutral, monomolecular species. The trimethylphosphine adduct is the only compound described here that can be handled at room temperature. The ^{31}P, ^{19}F, and ^{1}H nmr spectra data for these phosphine adducts are given in Table I. The nmr spectra for $Me_3P \rightarrow PF_5$ were obtained at 37° in CH_3CN solution; at −10° in CH_2Cl_2 for $HMe_2P \rightarrow PF_5$; and at −75° in CH_3Cl solution for $H_2MeP \rightarrow PF_5$.

The nmr data for each of these compounds are consistent with an adduct which ostensibly contains both octahedral and tetrahedral phosphorus atoms (Figure 1). Four equivalent fluorine atoms lie in the equatorial plane of the octahedrally coordinated phosphorus atom with a unique fluorine atom in an axial position, colinear with the P–P bond. Hereafter, the octahedral phosphorus atom will be designated P_α and the tetrahedral phosphorus P_β.

The general appearance of the ^{19}F spectrum of each compound is as shown in Figure 2. The data are similar to those reported for $Me_3N \rightarrow PF_5$.[1,2] The equatorial fluorines are found at lower field, the resonance being split into doublets by P_α, P_β, and F_{ax} to give a total of eight lines. At smaller sweep widths, all eight lines in the equatorial fluorine region appear to be without fine structure, but at the same sweep widths each line is split into a doublet for the dimethylphosphine compound and a triplet for the methylphosphine compounds due to $^3J_{FH}$ coupling. The smaller couplings with the methyl hydrogens ($^4J_{FH}$) were not resolved.

The axial fluorine is found at higher field (Figure 2) and is split into a large doublet by P_α and further into a 1:4:6:4:1 quintet by the four equivalent equatorial fluorines. A significant feature of the ^{19}F nmr spectra of these compounds is the absence of P_β–P–F_{ax} coupling. To our knowledge, phosphine adducts of phosphorus pentafluoride represent the first examples of a linear P–P–F moiety. By contrast the P_β–P–F_{eq} coupling (nominally a 90° geometry) approximates

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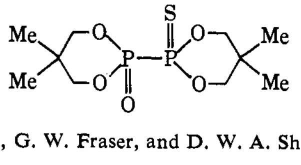
[5] (a) E. G. Finer and R. K. Harris, *Chem. Commun.*, 110 (1968); (b) R. K. Harris, J. R. Woplin, J. Michalski, and W. Stec, *ibid.*, 1391 (1970), subsequent to the acceptance of this manuscript, reported another $^1J_{PP}$ = +475 Hz for the compound



[6] D. H. Brown, G. W. Fraser, and D. W. A. Sharp, *J. Chem. Soc. A*, 171 (1966).

[7] J. S. Harman and D. W. A. Sharp, *ibid.*, *A*, 1138 (1970).

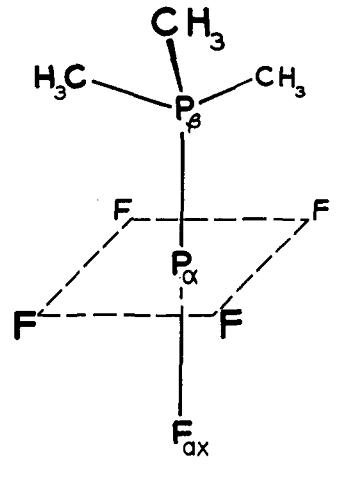


Figure 1. Idealized geometry of $Me_3P \rightarrow PF_5$.

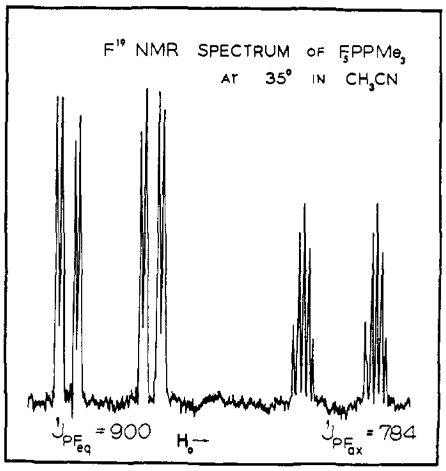


Figure 2. ^{19}F nmr spectrum of $Me_3P \rightarrow PF_5$.

+200 Hz. The intermediate P–P–F geometry in compounds such as F_2PPF_2 or F_2PPH_2 gives couplings on the order of +65 to +80 Hz.[8,9] There also was a lack of coupling through the linear P–P–F linkage for the longer range $^3J_{HF_{ax}}$, but F_{eq}–P–P–H coupling constants of 6.5 and 7.7 Hz were observed in the ^{19}F spectra for the dimethylphosphine and methylphosphine complexes, respectively.

The ^1H nmr spectral data of the three alkylphosphine adducts are also given in Table I. Only partial data are reported for the methylphosphine adduct because of the difficulty in finding the P–H signal of the dilute sample in the region of the strong solvent lock. The 60-MHz ^1H nmr spectrum of $Me_3P \rightarrow PF_5$ is shown in Figure 3 and the 100-MHz spectrum of $HMe_2P \rightarrow PF_5$ is shown in Figure 4. The $^1J_{PH}$ value of 425 Hz for $HMe_2P \rightarrow PF_5$ is somewhat smaller than most other four-coordinate phosphorus compounds.[10]

The ^{31}P nmr spectral data of $Me_3P \rightarrow PF_5$ and $HMe_2P \rightarrow PF_5$ are also given in Table I. Saturated solutions of $H_2MeP \rightarrow PF_5$ in CH_3Cl were too weak to be studied with our ^{31}P nmr facilities. Solutions of $HMe_2P \rightarrow PF_5$ in CH_2Cl_2 actually gave the strongest signals in spite of the fact that more lines are present than in the case of the trimethylphosphine complex. In both cases, the P_β region of the spectrum was much easier to interpret than the P_α region. The $^1J_{PP}$ coupling constants of 715 and 725 cps are the largest reported values for directly bonded phosphorus atoms. The other spin–spin coupling data are not unique to the ^{31}P nmr spectrum and they are more accurately obtained from the other spectra.

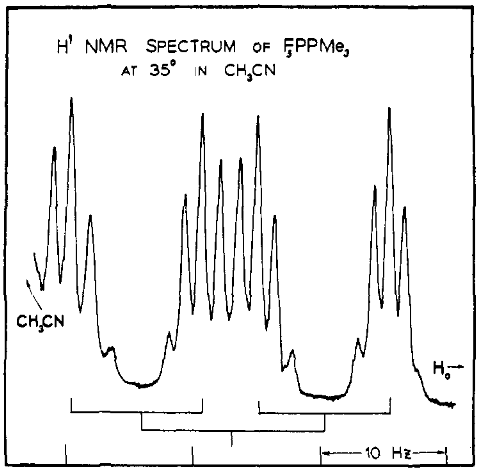


Figure 3. ^1H nmr spectrum (60 MHz) of Me_3PPF_5. The brackets denote splitting patterns.

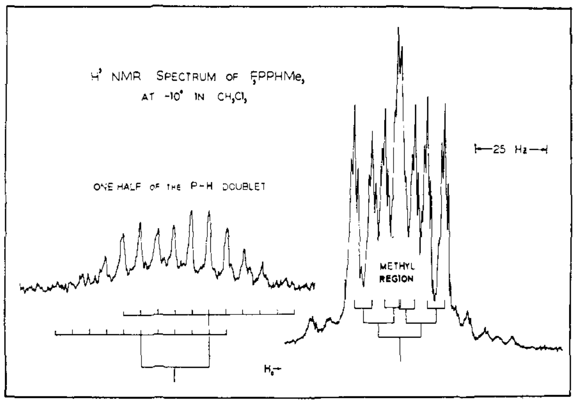


Figure 4. ^1H nmr spectrum (100 MHz) of $HMe_2P \rightarrow PF_5$. The brackets denote splitting patterns. Each half of the P–H doublet is interpreted as overlapping 11-line multiplets. Each 11-line grouping arises from the overlap of quintets of septets ($^3J_{HF} = {}^3J_{HH}$).

Only the center three members of two quintets in the P_β region could be identified in the case of $Me_3P \rightarrow PF_5$. This pattern results from splitting of the P_β resonance into a large doublet by P_α, each member of which is split into a smaller quintet by four equivalent equitorial fluorine atoms. The even smaller $^2J_{PCH}$ coupling which would also be expected could not be resolved because of the weakness of the sample.

In comparison to $Me_3P \rightarrow PF_5$, the presence of the directly bound hydrogen was confirmed in the case of HMe_2PPF_5 by an additional doubling of the P_β region ($^1J_{PH}$ = 416 Hz). Also, at smaller sweep widths, the stronger lines could be resolved into septets which are attributable to coupling with the six methyl hydrogens.

The splitting pattern of the octahedrally coordinated phosphorus atom in $HMe_2P \rightarrow PF_5$ was too complex to

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(8) R. W. Rudolph and R. A. Newmark, *J. Amer. Chem. Soc.*, **92**, 1195 (1970).

(9) R. W. Rudolph and H. W. Schiller, *ibid.*, **90**, 3581 (1968); unpublished results.

(10) S. O. Grim and W. McFarlane, *Can. J. Chem.*, **46**, 2071 (1968).

interpret by inspection. But by using the pertinent couplings from the ^{19}F and ^{1}H nmr, and the $^{1}J_{PP}$ value derived from the P_{β} region of the ^{31}P spectrum, it was possible to construct graphically the expected intensity patterns and identify all the major couplings.

The observed chemical shifts of the phosphorus nuclei in each compound are in the expected ranges for four- and six-coordinate phosphorus compounds.[11]

Stability. No evidence of decomposition of the trimethylphosphine adduct at room temperature *in vacuo* has been found. The compound is essentially insoluble in ether, THF, CS_2, $CFCl_3$, CCl_4, and $CHCl_3$. It is slightly soluble in CH_2Cl_2. Acetonitrile was the best solvent found for the adduct. No evidence has been found that the CH_3CN replaces the phosphine in the adduct. The compound is moderately resistant to hydrolysis in that after being exposed to the atmosphere for 1 week, only a few additional weak lines appear in the X-ray powder diffraction pattern and ^{1}H nmr spectrum. However, mass spectroscopic data on samples exposed to the atmosphere reveal significant amounts of water and POF_3. Similar to phosphoranes,[12] the parent peak was not observed in the mass spectrum. The highest observed *m/e* value was 183, which results from $Me_3P \rightarrow PF_4^+$.

Without a solvent, $HMe_2P \rightarrow PF_5$ decomposes very slowly at +5°, but rapidly at room temperature. A 1.6-mmol sample was completely decomposed within 2 hr when at +27°. The complex is moderately soluble in methylene chloride and acetonitrile.

The decomposition of $HMe_2N \rightarrow PF_5$ at 100-120° provides a method of preparing the dialkylaminophosphorane *via* the elimination of HF.[6]

$$2HMe_2N \rightarrow PF_5 \longrightarrow PF_4NMe_2 + H_2NMe_2^+PF_6^-$$

The corresponding dimethylphosphonium salt has been identified from the ^{31}P and ^{1}H nmr solutions of the decomposition products of $HMe_2P \rightarrow PF_5$. The interesting compound F_4PPMe_2 which might also be expected as a product of this reaction has not yet been isolated. Phosphorus trifluoride is the only fragment of this molecule which has been recovered. An investigation of this decomposition reaction is continuing.

The methylphosphine adduct was the least stable compound described here. Without a solvent, it is stable at −78° and decomposes only slowly at −45°, but quickly at −22°. The relatively high melting point of acetonitrile precluded its used as a solvent for this compound. It is only slightly soluble in methyl chloride and methylene chloride at −78°. The decomposition products of this compound which have been identified are $[H_3PCH_3]^+PF_6^-$ and PF_3.

The facile decomposition of $HMe_2P \rightarrow PF_5$ and $H_2MeP \rightarrow PF_5$ is probably not so much a reflection of the strength of the P–P bond as it is of the ease of elimination of HF from these molecules. A more accurate indication of the relative strength of the coordinate bond was obtained from base displacement studies involving trimethylamine and trimethylphosphine with respect to the Lewis acid PF_5. These equilibrium studies demonstrated that trimethylphosphine is a significantly stronger base.[13] The equilibrium constant, which was approached from each direction, for the reaction

$$Me_3N \rightarrow PF_5(s) + Me_3P(g) \rightleftharpoons Me_3P \rightarrow PF_5(s) + Me_3N(g)$$

was 5.5 ± 1.5 at 27°.

Previous investigations which were based on reactivity showed that amines form kinetically more stable complexes with BF_3 than with PF_5.[1] However, the thermochemical investigations of Holmes, *et al.*, indicated the opposite relative acidity[14] with pyridine as a reference base, *i.e.*, $PF_5 > BF_3$. In order to establish the relationship of PMe_3 to BF_3 and PF_5, the equilibrium

$$Me_3P \rightarrow BF_3(s) + PF_5(g) \rightleftharpoons Me_3P \rightarrow PF_5(s) + BF_3(g)$$

was approached from both sides.[13] The equilibrium constant of 6.6 ± 1 at 29° indicates that BF_3 is a weaker acid toward PMe_3 than is PF_5 in accord with the suggestion of Holmes, *et al.*[14]

The coordinate bond strength established here ($P \rightarrow P > N \rightarrow P$) may be a reflection of the acidity of PF_5. If the latter is the correct interpretation, other less acidic phosphorus(V) fluorides such as $MePF_4$ might show the opposite order ($N \rightarrow P > P \rightarrow P$). Shore has noted that the $P \rightarrow B$ coordinate bond becomes stronger than the $N \rightarrow B$ bond as the strength of the acid increases.[15] However, the latter study involved only donor→B bonds and the present case involves donor→P bonds. The ability of phosphorus to coordinate effectively at a greater distance must also be considered. The P–P bond is strikingly constant at about 2.22 Å length,[4] but the P–N single-bond length is a much shorter 1.769 Å.[16] If the latter steric requirement is considered, the observed strength of the $P \rightarrow P$ bond *vis-á-vis* the $N \rightarrow P$ bond is not surprising.

P–P Coupling. In order to determine the sign of $^{1}J_{PP}$, high-resolution, frequency-sweep spectra were taken of the eight lines comprising the F_{eq} region of the ^{19}F spectrum (Figure 2) while simultaneously irradiating the Me_3P region of the ^{31}P spectrum. By systematically incrementing the decoupling frequency by 20 Hz the effects outlined in Table II were observed. This manually scanned indor spectrum of the Me_3P region of the phosphorus spectrum shows six decoupling regions related by 720 ± 20[17] and 180 ± 20 Hz[17] ($^{1}J_{PP}$ and

Table II. Decoupling Results[a]

Decoupling frequency, Hz A	 B
40, 477, 100[b]	40, 476, 350[b]
40, 477, 270[c]	40, 476, 540[c]
40, 477, 450[b]	40, 476, 725[b]

[a] Affected lines in F_{eq} region are (A) four low-frequency lines, (B) four high-frequency lines. [b] A moderate decoupling effect was noted at this frequency. [c] A strong decoupling effect was noted at this frequency.

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(11) M. M. Crutchfield, C. H. Dungan, J. H. Letcher, V. Mark, and J. R. Van Wazer, *Top. Phosphorus Chem.*, 5, 173 (1967).

(12) T. A. Blazer, R. Schmutzler, and I. K. Gregor, *Z. Naturforsch. B*, 24, 1081 (1969).

(13) In the heterogeneous systems studied it was assumed that crystal lattice contributions and entropy contributions were negligible.

(14) R. R. Holmes, W. P. Gallagher, and R. P. Carter, Jr., *Inorg. Chem.*, 2, 437 (1963).

(15) D. E. Young, G. E. McAchran, and S. G. Shore, *J. Amer. Chem. Soc.*, 88, 4390 (1966).

(16) E. Hobbs, D. E. C. Corbridge, and B. Raistrick, *Acta Crystallogr.*, 6, 621 (1953); D. W. Cruickshank, *ibid.*, 17, 671 (1964).

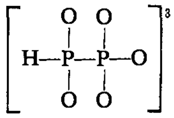
(17) A more precise location of the ^{31}P resonance centers in these indor experiments was seriously compromised by the splitting of each line into a dectet by the nine methyl hydrogens ($^{2}J_{PH} = 13.5$ Hz).

${}^2J_{PF_{eq}}$, respectively). The outer members of the anticipated pair of quintets could not be detected because of their relatively weak indor effect.

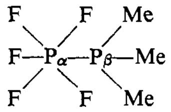
When any one of the low-frequency ${}^{31}P$ lines was irradiated, the four high-frequency lines in the ${}^{19}F$ spectrum were perturbed,[18] and *vice versa*. Thus, ${}^1J_{PF_{eq}}$ and ${}^1J_{PP}$ are opposite in sign.[19] Since the absolute sign of the directly bonded PF coupling is negative,[20-22] ${}^1J_{PP}$ in Me_3PPF_5 is positive. Similar experiments were not performed with HMe_2PPF_5 and H_2MePPF_5, but ${}^1J_{PP}$ is certainly positive in these cases, too. Similar indor experiments in which the P_α region was irradiated and the F_{eq} region observed showed that ${}^2J_{PF_{eq}}$ is positive and ${}^2J_{FF}$ is negative in these compounds.

Finer and Harris first suggested a sign variation in order to explain the large range in magnitude of ${}^1J_{PP}$.[5] In support of this contention they measured the first positive directly bonded P–P coupling [+465.5 Hz for $(HP_2O_5)^{3-}$]. Important to their extension of the theory given by Pople and Santry[23] was a positive sign for ${}^1J_{PP}$ in F_2PPF_2. While the calculations of Cowley and White[24] supported the contention of a positive ${}^1J_{PP}$ in tetrafluorodiphosphine, a recent double-resonance experiment showed the sign to be negative.[8] It is now clear that when the P–P bond contains at least one P atom having a lone pair of electrons, the coupling constant is negative and greater in magnitude than 100 Hz[25] (Table III). On the other hand, for "singly bonded" P atoms the known signs are positive (Table III).

The fact that the directly bonded P–P coupling for Me_3PPF_5 is the largest such value reported, and is positive as opposed to the negative values reported for most other P–P bonds, has some interesting implications regarding the mechanism of spin–spin coupling in the P–P bond. Although coupling can be transmitted by a Fermi-contact effect, an orbital effect, and a spin-dipolar effect,[23] the latter two contributions are usually neglected.[23,26] However, Blizzard and Santry recently demonstrated the importance of the orbital and spin-dipolar terms in certain cases.[26] The orbital and spin-dipolar contributions, which depend largely on π-type orbitals,[23,26] should be negligible in the case of the single P–P bonds found in

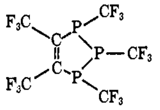
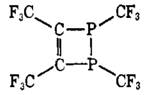
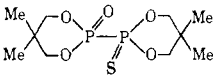


and



However, the large range in "single-bond" P–P couplings (Table III) and lack of more sign determinations makes the assumption that all such couplings are positive premature at this time.

Table III. P–P Coupling Constants

	${}^1J_{PP}$[a]	Ref
Molecules with a "Formal" $>\ddot{P}-\underset{\cdot\cdot}{P}<$ Bond		
$LiEt\ PP(C_6H_5)Et$	396	*b*
$P(PF_2)_3$	323	*c*
$K(Et)P—P(Et)—P(Et)K$	306	*b*
$Et_2PP(C_6H_{11})_2$	282	*d*
$(CF_3)_2PPMe_2$	−256	*e*
$F_2PP(CF_3)_2$	234	*f*
F_2PPF_2	−230	*g*
$(C_6H_5)_2PP(C_6H_{11})_2$	224	*d*
	220	*h*
$Li(C_6H_5)P[P(C_6H_5)]_2P(C_6H_5)Li$	216	*a*
F_2PPH_2	−211	*f, i*
Me_2PPMe_2	−179.7	*j*
H_2PPH_2	−108	*k*
	55	*h*
Molecules with a "Formal" $>\ddot{P}-P\lessdot$ Bond		
$[Cl(Me_2N)PP(NMe_2)_3]^+$	350	*l*
$[Me_2N)_2PP(NMe_2)_3]^+$	350[m]	*l*
$(CF_3)_2PPF_2BH_3$	316	*f*
$H_2PPF_2BH_3$	−255	*f*
$(C_6H_5)_2PP(O)(C_6H_5)_2$	224	*n*
$Me_2PP(S)Me_2$	−220	*o*
$C_6H_5(MeO)P(O)—P(C_6H_5)—P(O)(OMe)C_6H_5$	210	*n*
$(C_6H_5)_2P—P(O)(OEt)C_6H_5$	205	*n*
$MeO(C_6H_5)P—P(O)(OMe)_2$	202	*n*
$Cl(C_6H_5)P—P(O)(C_6H_5)_2$	202	*n*
$EtO(C_6H_5)P—P(O)(OEt)_2$	201	*n*
$(C_6H_5)_2P—P(O)(OMe)_2$	192	*n*
$(C_6H_5)_2P—P(O)(OEt)_2$	178	*n*
$(MeO)_2P(O)—P(C_6H_5)—P(O)(OMe)_2$	168	*n*
Molecules with "Singly Bonded" P Atoms		
$Me_3P\rightarrow P—F_5$	+715	This work
$HMe_2P\rightarrow P—F_5$	+723	This work
$(Et_2O)_2(S{=})P—P({=}O)(OEt_2)_2$	583	*p*
	+475	*q*
$[O_3—P—P—O_2H]^{3-}$	+465.5	*q*
$Me_2(S{=})P—P({=}S)Me_2$	18.7	*o*
$Et_2(S{=})P—P({=}S)(c\text{-}C_6H_{11})_2$	69	*d*

[a] In hertz. The sign of the coupling is given if it has been determined. [b] E. Fluck and K. Issleib, *Z. Anorg. Allg. Chem.*, **339**, 274 (1965). [c] D. Solan and P. L. Timms, *Chem. Commun.*, 1540 (1968). [d] E. Fluck and K. Issleib, *Chem. Ber.*, **98**, 2674 (1965). [e] S. L. Mannatt, D. D. Elleman, A. H. Cowley, and A. B. Burg, *J. Amer. Chem. Soc.*, **89**, 4544 (1967). [f] Reference 9b. [g] Reference 8. [h] W. Mahler, *J. Amer. Chem. Soc.*, **86**, 2306 (1964). [i] Reference 9. [j] E. G. Finer and R. K. Harris, *Mol. Phys.*, **13**, 65 (1967). [k] R. M. Lynden-Bell, *Trans. Faraday Soc.*, **57**, 888 (1961). [l] C. W. Schultz, Ph.D. Thesis, University of Michigan, 1969. [m] Temperature dependent. [n] E. Fluck and H. Binder, *Inorg. Nucl. Chem. Lett.*, **3**, 307 (1967). [o] R. K. Harris and R. G. Hayter, *Can. J. Chem.*, **42**, 2282 (1964). [p] R. K. Harris, A. R. Katritzky, S. Musierowicz, and B. Ternai, *J. Chem. Soc. A*, 37 (1967). [q] Reference 5.

More is known regarding P–P bonds where there is the possibility of p_π–d_π bonding. A calculation for

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[18] Four lines are perturbed simultaneously since ${}^2J_{PF_{ax}} = 0$. In the limit where ${}^2J_{PF_{ax}} > {}^2J_{PH} = 0$ the signs of ${}^2J_{F_{eq}F_{ax}}$ and ${}^2J_{PF_{ax}}$ could be related by the experiment described and in this case only two lines (related by ${}^2J_{PF_{eq}}$) would be perturbed when a ${}^{31}P$ line is irradiated.

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[25] The one known exception to this, 1,2,3,4-tetrakis(trifluoromethyl)-3,4-diphosphacyclobutene, probably derives from a strained P–P bond.

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F_2PPF_2, based *only* on the Fermi-contact effect, gave ${}^1J_{PP} = +707.36$ Hz for the trans structure.[24,27] Although the sign and magnitude of the latter are in disagreement with the experimental value (-230 Hz[8]), if the calculation is a correct estimate of the contact contribution to ${}^1J_{PP}$, the value observed for F_2PPF_2 may be due to the dominance of a negative contribution by one or both of the other terms. Thus, since all known couplings are negative where at least one P atom in the P–P bond has a lone pair of electrons, it is tempting to speculate that the contact effect is not dominant.[29a] However, this proposal must be held with some reservation until more estimates of the contact contribution are available,[29b] since it too may vary in sign due merely to a change in the symmetry of the dominant electronic transition of the P–P bond.[23,30,31]

Experimental Section

General. Vacuum line techniques were used for the manipulation and purification of reactants.[32] When samples were prepared for Raman spectra and X-ray photographs, the compounds were handled in a nitrogen-atmosphere glove bag. Reactions were carried out in 25–35-cm^3 vessels which could be attached to the vacuum system through an O-ring joint and sealed with a Fisher-Porter 4-mm, quick opening, Teflon stopcock. Nmr tubes were attached to the vessels just below the stopcock in a vertical position so that the entire vessel (up to the stopcock) could be submerged in a 1-l. dewar. In the case of unstable species, solvent was distilled in and the entire vessel submerged in a $-78°$ slush. To obtain nmr samples the vessel was removed from the cooling bath and the solution was quickly poured into the nmr tube. The nmr tubes were sealed off with their contents at low temperature and *in vacuo*.

Adduct Formation. Tensimetric titrations[32] of $P(CH_3)_3$ in methylene chloride or $HP(CH_3)_2$ and H_2PCH_3 without a solvent at $-78°$ with PF_5 showed an inflection at *only* a molar ratio of 1:1 which indicates the formation of a single adduct

$$1.0\mathrm{PF_5} + 1.0\mathrm{H}_n\mathrm{P(CH_3)}_{3-n} \xrightarrow{-78°} 1.0\mathrm{PF_5{:}H}_n\mathrm{P(CH_3)}_{3-n}$$

where $n = 0$, 1, and 2.

Combinations of the reactants in nonstoichiometric amounts without a solvent in the vacuum line produce the adduct and the expected amount of recoverable, excess reactant.

In a typical preparation of Me_3PPF_5, equimolar quantities of the reactants are condensed into a reaction vessel at $-196°$ and allowed to warm to room temperature. The reaction begins as the trimethylphosphine melts with the formation of a white crystalline solid. The infrared spectrum of the solid as a KBr pellet consisted of the following absorptions: 3015 (w), 2935 (w), 1445 (sh, w), 1425 (s), 1305 (m), 1292 (m), 995 (s), 805 (vs), 682 (vw), 650 (s), 532 (s), and 350 (m) cm^{-1}. The Raman spectrum obtained from the finely divided powder in a sealed capillary is: 3019 (ms), 2941 (s), 1436 (m), 807 (w), 776 (m), 691 (m), 668 (s), 572 (w), 545 (w), 373 (m), 283 (m), 237 (s), and 130 (m) cm^{-1}. The X-ray powder diffraction pattern consisted of the following d values and intensities: 5.6 (s), 4.7 (s), 3.62 (m), 3.41 (m), 2.89 (vw), 2.76 (w), 2.49 (m), 2.40 (m), 2.21 (m), 1.995 (vw), 1.958 (vw), 1.850 (vw), 1.824 (w), 1.805 (w), 1.605 (vw), 1.590 (w), 1.532 (vw), 1.464 (vw), 1.448 (vw), 1.390 (vw), 1.379 (vw), 1.343 (vw), 1.325 (vw), and 1.280 (vvw). The unit cell is tentatively assigned as primative tetragonal with $a = 4.23$, $c = 11.0$.

In a typical preparation of HMe_2PPF_5 or H_2MePPF_5, equimolar quantities of the phosphine and phosphorus pentafluoride are condensed into a reaction vessel connected to the vacuum line at $-196°$ and then quickly warmed to $-78°$. The reactions occur at such a rate that very little PF_5 pressure is observed on a manometer opened to the vessel. White solid product is formed.

Equilibrium Studies. The relative base strengths of trimethylphosphine and amine toward phosphorus pentafluoride were determined by studying the infrared spectra of the gases in the systems

$$\mathrm{Me_3N{\rightarrow}PF_5(s) + Me_3P(g) \rightleftarrows Me_3P{\rightarrow}PF_5(s) + NMe_3(g)}$$

$$\mathrm{Me_3P{\rightarrow}PF_5(s) + Me_3N(g) \rightleftarrows Me_3N{\rightarrow}PF_5(s) + PMe_3(g)}$$

Equimolar quantities of the phosphine and amine were used in each reaction studied. Concentrations of the gases were determined by comparing the observed absorbance of the 840-cm^{-1} line of NMe_3 and the 950-cm^{-1} line of PMe_3 to calibration curves based on the pressure in the ir cell. The equilibrium constant is independent of volume and the concentrations are directly proportional to the partial pressures. The total pressure in the 71-mm ir cell was 80 mm. The slowly established solid–gas equilibrium was monitored daily and required over 3 weeks for the 2-mmol samples to come to equilibrium [$K_{eq} = p(NMe_3)/p(PMe_3)$].

The BF_3–PF_5 equilibrium study was performed similarly. The BF_3 partial pressure was determined from the intensity of the 1385-cm^{-1} absorbance. The PF_5 partial pressure was determined from the difference between P_{BF_3} and the total pressure.

Starting Materials. Methyl-, dimethyl-, and trimethylphosphine were prepared and purified by literature methods.[33] Phosphorus pentafluoride was obtained from Ozark Mahoning and purified by distillation through -111, -150, and $-196°$ traps. The material in the $-150°$ trap consisted of mainly PF_5 with *ca.* 1% POF_3 (ir). The PF_5 was enriched by rapid distillation through -83, -95, and $-111°$ traps. The material in the $-111°$ trap was used. Acetonitrile was dried over molecular sieves and distilled through -30, -45, and $-196°$ traps. The material in the $-45°$ trap was used. Methylene chloride was stored over molecular sieves and distilled through -63, -78, and $-196°$ traps. The material in the $-78°$ trap was used. Methyl chloride was obtained from the Matheson Co. and distilled through a $-95°$ trap prior to use.

Instrumentation. Infrared spectra were obtained in a gas cell with KBr windows or as KBr pellets with a Wilks Minipress on a Beckman IR-10. Raman spectra were obtained on a Spex 1401 spectrometer using an argon laser. A General Electric XRD X-ray generator using nickel-filtered Cu Kα radiation was used to determine the powder diffraction patterns. Mass spectra were determined with a Picker MS-9 mass spectrometer.

Nmr spectra were recorded by using the appropriate probe with Varian HA-100 and T-60 instruments. In order to effect heteronuclear spin tickling, the output from a General Radio 1164-AR7C frequency synthesizer was fed directly to a Varian V-4333 probe using the double tuning scheme described by Burton and Hall.[34] Experiments were performed with a saturated solution of Me_3PPF_5 in CH_3CN containing *ca.* 15% by volume $CFCl_3$ for the lock signal.

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(27) The trans configuration was originally suggested for F_2PPF_2 on the basis of vibrational spectroscopy;[28] a preliminary analysis of electron diffraction data is not inconsistent with this suggestion: L. S. Hodges and L. S. Bartell, unpublished results.

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