

Figure 5. Difference visible absorption spectra of the complexes of soybean lipoxygenase with 4-nitrocatechol (—) and methyl protocatechuate (---) vs. oxidized lipoxygenase in 0.1 M potassium phosphate buffer pH 7.0 under N_2 at 5 °C.

EPR studies on the NO complex of Fe(II) lipoxygenase suggest that there is only one site for exogenous ligand binding;³⁸ upon binding, catechol probably occupies this exogenous ligand site and displaces an endogenous ligand as well. The endogenous ligands proposed for phenylalanine hydroxylase and soybean lipoxygenase are also those found in the active site of iron superoxide dismutase.^{39,40} Such a ligand set would favor the Fe(II) oxidation state,

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yet still allow ready access to the Fe(III) state. In keeping with its function, the iron center of superoxide dismutase is well-poised electrochemically to be reduced by superoxide in the Fe(III) form and to be oxidized by superoxide in the Fe(II) form.

The roles of the metal centers of phenylalanine hydroxylase and lipoxygenase are not yet understood. For phenylalanine hydroxylase, the iron center may be the site for oxygen binding and its subsequent activation. The ligand environment may allow the iron center to shuttle between Fe(II) and Fe(IV) oxidation states for the hydroxylation reaction. Such a mechanism would differ from the formally Fe(III)/Fe(V) shuttle proposed for the cytochrome P450 mechanism.⁴¹ For lipoxygenase, a current hypothesis for the enzyme mechanism involves deprotonation and oxidation of the 11- CH_2 of the 9,12-diene unit to yield an intermediate bis-allyl radical (or equivalent iron-coordinated species) that may then react with dioxygen.⁴² The active site of lipoxygenase may have evolved so as to stabilize Fe(II), resulting in an Fe(III)/Fe(II) potential appropriate for the oxidation of the diene. The work reported here provides a starting point for elucidating the role of the metal in these oxygenation reactions.

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(40) We have attempted the analogous catechol binding experiment with the iron superoxide dismutase from *E. coli* and were unable to form a complex. Dr. J. A. Fee (personal communication) has informed us that he was also unable to form the catechol complex. It is likely that catechol cannot gain access to the active site of superoxide dismutase because of the nature of the active site cleft. In contrast, both phenylalanine hydroxylase and lipoxygenase can accommodate the catechol presumably because of its similarity to the substrates.

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The Nature of the Phosphorus-Phosphorus Double Bond As Studied by Solid-State NMR

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Abstract: The nature of the P=P double bond in 1,2-bis(2,4,6-tri-*tert*-butylphenyl)diphosphene (**1**) has been studied by static and magic angle spinning ³¹P solid state NMR. MAS spectra of **1** give an isotropic shift of +494 ppm relative to 85% orthophosphoric acid. Static powder spectra show an exceptionally large shift anisotropy with $\sigma_{11} = 1236$, $\sigma_{22} = 249$, and $\sigma_{33} = -3$ ppm. A two-dimensional NMR method has been applied which separates the dipolar coupling between the two ³¹P nuclei from the chemical shift anisotropy and permits assignment of the orientation of the shift tensor in the molecular frame. The component at high field is approximately perpendicular to the CPP plane, and the low field component is in this plane and perpendicular to the direction of the phosphorus lone pair. By using the known bond length, the anisotropy in the indirect dipolar or scalar coupling between the two ³¹P centers is also determined. These results are compared with the solid state spectra for 1,2-bis(2,4,6-tri-*tert*-butylphenyl)diphosphene (**2**) and 2,4,6-tri-*tert*-butylphenylphosphine (**3**). A comparison of these results with previous work on olefins and disilenes shows that the P=P double bond is similar in many respects to the double bonds formed by group IV elements.

Interest in multiply bonded compounds of the heavier main group elements has increased rapidly in the last 10 years as more

and more examples of these species have been synthesized and characterized.² During this time the first examples of stable

compounds with, e.g., Si=Si,³ P=P,⁴ As=As,⁵ Ge=Ge,⁶ Sn=Sn,⁷ and Ge=P⁸ double bonds were secured culminating many years of attempts to isolate such derivatives. Considerable activity² is now aimed at developing the chemistry of main group dimetallenes and in characterizing them both experimentally and theoretically. In this paper we report on the first use of solid state ³¹P NMR methods to investigate the nature of the P=P bond in 1,2-bis(2,4,6-tri-*tert*-butylphenyl)diphosphene (**1**). Although considerable effort has been expended in characterizing diphosphenes, relatively little is known about the detailed description of the P=P bond. Both Raman^{10b} and X-ray diffraction methods have been used so far to study this system. In the X-ray structure⁴ of **1** the phosphorus-phosphorus distance is 2.034 Å and thus approximately 9% shorter than that of a typical diphosphine. This is in close parallel with the differences found between single and double bonds between carbons or silicons⁹ and is in agreement with quantum mechanical calculations¹⁰ for model systems. This evidence indicates that the P=P bond is similar in this respect to C=C and Si=Si bonds.

It is now well established that the anisotropy of the chemical shift (CSA) a nucleus experiences is a very sensitive measure of the three-dimensional electronic structure of its surroundings.¹¹⁻¹⁴ Just as a large anisotropy in magnetic susceptibility has been used as a characteristic property accompanying aromaticity,¹⁵ large shift anisotropies have been shown to be a characteristic of multiple bonding arrangements for ¹³C and ²⁹Si.^{13,14} The work reported here extends this correlation to bonding in phosphorus-containing compounds. In **1** the CSA is found to be over 13 times that in 1,2-bis(2,4,6-tri-*tert*-butylphenyl)diphosphine (**2**) and 2,4,6-tri-*tert*-butylphenylphosphine (**3**). Static and magic angle spinning (MAS) cross polarization (CP) methods have been used with spin echo techniques to acquire these ³¹P spectra. The direct and indirect dipolar interactions in **1** were also investigated by a

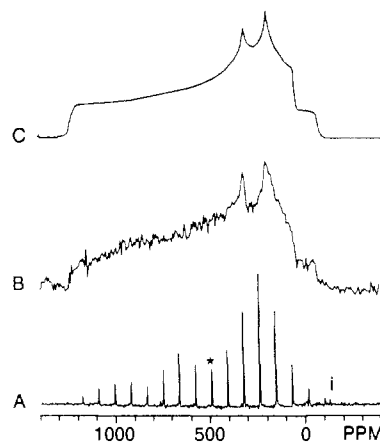


Figure 1. (a) ³¹P MAS spectrum of **1**. * marks the isotropic shift; i is an impurity. (b) ³¹P powder spectrum of **1**. (c) Simulation of b using parameters given in the text.

two-dimensional (2D) NMR method as well as by the modulation of Carr-Purcell-Meiboom-Gill spin echo trains. In combination with quantum mechanical calculations, these data permit an assignment of the ³¹P shift tensor in **1** to the molecular frame and provide a basis for comparison with C=C and Si=Si double bonds.

Experimental Section

Compounds **1-3** were prepared as described previously.¹⁶ For the powder NMR measurements all samples were kept in 3-cm long sealed NMR tubes of 10-mm diameter. For MAS spectra the samples were transferred in an inert atmosphere glovebag to MAS rotors constructed of hot-pressed boron nitride. The cylindrical sample cells were closed with a threaded Kel-F cap and stored in vials under nitrogen when not in use. None of the samples were observed to change over a period of several months when handled in this manner. In the MAS experiments dry nitrogen was used to operate the spinner turbine to further ensure the integrity of the samples.

Spectra were collected with a homebuilt NMR spectrometer similar to that described in ref 17. This spectrometer is equipped with a 2.35 T superconducting solenoid giving a ³¹P resonance frequency of 40,466 MHz. Although much higher field strengths were available, the lower operating frequency was advantageous for this work due to the extremely large shift anisotropies encountered. A single coil doubly tuned MAS probehead of our own design¹⁸ was used in all experiments. In MAS experiments the spin rates were typically in excess of 3.5 kHz. Hartmann-Hahn matched cross polarization between protons and ³¹P with radio frequency field amplitudes of approximately 17 G were used to collect all spectra, and several hundred or thousand scans were typically required. In all powder spectra the cross polarization period was followed by a spin echo to avoid probe and receiver recovery problems. This was found to be absolutely necessary in acquiring spectra of **1** without gross distortion of the line shape. In some MAS experiments a spin echo sequence with the π pulse timed to occur exactly one rotor cycle after the cross polarization period^{19,20} was also found to be useful for the same reasons. Phosphorus shifts were referenced to external 85% orthophosphoric acid and are estimated to be accurate to within ± 0.5 ppm unless otherwise indicated.

In order to interpret the powder NMR results for **1** the contributions of the direct dipolar and indirect dipolar or scalar couplings were independently determined by using a two-dimensional (2D) NMR method. Following cross polarization the ³¹P spins were allowed to evolve for a time $t_1/2$, after which a π pulse was applied. After another time $t_1/2$, a spin echo forms as the chemical shifts are refocused. Since the dipolar interaction is not affected by the π pulse, the echo amplitude is modulated at the frequency of the dipolar couplings.²¹ The time t_1 was incremented sequentially in a 2D fashion to give a data set which correlates the chemical shift with the dipolar couplings. Echo modulation spectra using

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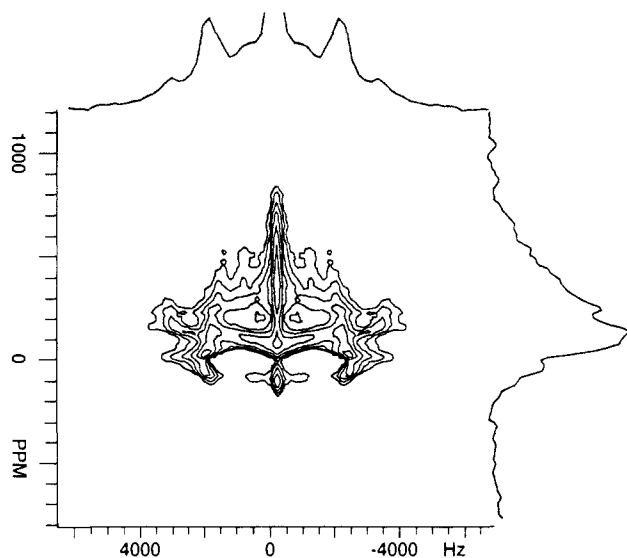


Figure 2. Contour plot of the 2D spin echo spectrum of **1**. Trace along the top is the summation of the data set onto the dipolar axis showing the Pake pattern observed when chemical shifts are suppressed. The spectrum along the side is the summation of the data set onto the chemical shift plus dipolar axis giving the same result as in Figure 1b.

a Carr–Purcell–Meiboom–Gill pulse train were also used for this purpose. In this experiment only the tops of the successive echoes are sampled giving an FID in which the chemical shifts are suppressed.²¹ The Fourier transform of this signal is a Pake doublet type of powder pattern determined by the direct and indirect dipolar couplings only.

For comparison with the experimentally observed CSA in **1**, independent gauge for localized orbitals (IGLO)²² calculations were carried out with use of 1,2-dimethyldiphosphene as a model system. In all calculations the basis set²³ for carbon (7s 3p) was contracted to (4111, 21) and that for hydrogen (3s) was contracted to (21). The best results were obtained with (11s 7p) contracted to (5111111, 31111) plus a d polarization function²³ with an exponent of 0.34 for phosphorus. The geometry of the CPPC skeleton was fixed to that determined by X-ray⁴ for **1** except that the CPPC moiety was restricted to a planar configuration. Simulations of powder spectra were calculated in a standard fashion.²⁴

Results

Figure 1 shows the results for compound **1** where trace B is the full powder spectrum for a static sample. This pattern is exceptionally wide, covering some 50 000 Hz from end to end. The extreme width of this spectrum posed experimental difficulties mentioned above which are not usually encountered in solid state NMR of dilute spin 1/2 nuclei. The line shape is also not a simple CSA powder pattern due to the additional effects of the direct and indirect dipolar couplings²⁴ between the two ³¹P nuclei in the P=P bond. Instead of three discontinuities corresponding to the three principal components of the shift tensor, this type of spectrum is characterized by six discontinuities of which five are clearly observed. The MAS results for **1** are depicted in Figure 1a. Because of the extreme width of this signal the MAS spectrum consists of a sideband pattern^{19,26} even at spin rates of 4 kHz. By using several spinning rates the centerband was found at a shift of +494 ppm in agreement with solution NMR measurements.¹⁶ The line width in the MAS spectrum is measured as 71 Hz full width at half height (fwhm) and is observed to be independent of the spinning rate from 800 to 4000 Hz.

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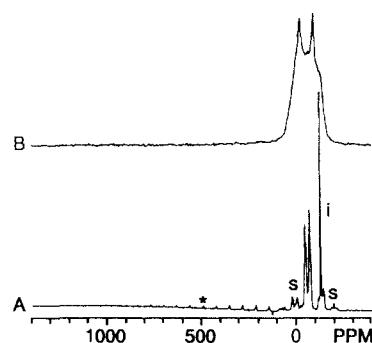


Figure 3. (a) ¹³P MAS spectrum of **2**. * marks isotropic shift of the **1** impurity in the sample, and i marks the impurity of **3**. s marks the spinning sidebands for **2**. The two lines centered about -57 ppm are attributed to **2**. (b) Powder spectrum of the same sample showing the small shift anisotropy that **2** exhibits in comparison to **1**.

The result of the chemical shift dipolar correlation 2D experiment is shown in Figure 2 as a contour plot. The vertical dimension here is the chemical shift plus dipolar frequency axis, and the horizontal axis corresponds to the dipolar only frequency scale. From the shape of the contours it can be seen that the dipolar coupling approaches zero at the low field end of the powder spectrum. This indicates that at this position in the spectrum the P=P bond is approximately at the magic angle from the static magnetic field (vide infra). The normal powder spectrum results from summing the data set onto the vertical axis and is shown on the right hand side of the contour plot. Along the top is a plot of the dipolar only powder spectrum produced by summing the data onto this axis. Similar patterns are obtained in the echo modulation experiment. The dipolar powder pattern can be fitted fairly well to an axially symmetric Pake line shape by using a splitting of 5600 Hz between the peaks of the pattern. These spectra do not display any measureable departure from axial symmetry, although the outermost wings of the pattern do not follow the expected intensities well. This is attributed to two experimental difficulties. First, it is not possible to obtain a good $t_1 = 0$ point because of receiver recovery problems, and this introduces a linear phase error which is not easy to correct for. This gives the effect of washing out the broad components of the line shape and enhancing the discontinuities as observed. The second problem encountered is that the RF fields used are not much larger than the full width of the powder pattern, thus giving a spread in effective field values across the band shape. This introduces more distortions into the dipolar spectrum as the π pulse then does not equally affect the spins at all points in the line shape.

Powder and MAS spectra for **2** were obtained to permit comparison of the shift anisotropy for a P–P single bond to that of the P=P double bond in **1**. In the MAS spectrum (Figure 3A) three major components are observed. The narrow peak (fwhm = 65 Hz) at -132 ppm is due to the presence of a small amount of the primary phosphine¹⁶ **3**. A trace amount of **1** is also apparent in this spectrum that is not evident in Figure 3B because the intensity is spread over a much wider band width in the static experiment. The two remaining lines at -68 and -46 ppm (fwhm = 360 Hz) account for the bulk of the integrated intensity in the MAS spectrum and are assigned to compound **2**. The average of these two shifts is -57 ppm in good agreement with the -59 ppm shift observed in solution.¹⁶ This type of solid state splitting effect is quite commonly observed in ¹³C MAS spectra and is most often due to intermolecular chemical shielding effects.³⁰ Further two-dimensional MAS NMR studies (to be published at a later date) have confirmed that the two resonances are attributable to two different pairs of slightly inequivalent phosphorus nuclei.

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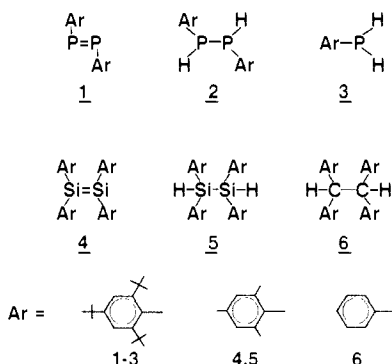
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These studies also indicate that these pairs are crystallographically inequivalent molecules in the same crystal and not simply two different crystalline modifications.

While the small amount of **1** present in this sample does not interfere with the powder spectrum for **2**, the impurity of **3** does as it has a relatively narrow powder pattern. This contribution



was subtracted out by using the powder spectrum recorded for a pure sample of **3** which gave an axially symmetric tensor with $\sigma_{11} = \sigma_{22} = -102$ ppm and $\sigma_{33} = -187$ ppm. The result of the spectral subtraction is shown in Figure 3B which is the powder spectrum for **2** alone. The CSA of **2** is in fact even smaller than indicated as this pattern also includes the phosphorus-phosphorus dipolar coupling. A simulation of this spectrum would require the CSA tensors for all four phosphorus nuclei involved, the pertinent direct and indirect dipolar tensors, and the relative orientations of these tensors. The resolution of the spectrum under consideration does not permit the determination of so many independent variables and as such a full fit was not considered fruitful. As a zeroth order approximation spectral simulations were carried out by using a single pair of phosphorus centers instead. The dipolar coupling assumed was appropriate for a typical P-P bond length of 2.23 Å, and the indirect dipolar couplings were omitted. Most of the features in the experimental spectrum could be simulated with a shift tensor having $\Delta\sigma = |\sigma_{11} - \sigma_{33}| = 90$ ppm and by using relative orientations of the tensor consistent with an approximate anti conformation for the diphosphine in the solid. Thus only about half of the total breadth of the powder pattern for **2** is due to the CSA contribution.

Static and slow spinning MAS ^{13}C spectra of 1,1,2,2-tetra-phenylethane were also acquired for comparison to **2** and **4**. In the slow spinning MAS experiment the observed line widths were sufficiently broad that the spinning sidebands for the aliphatic carbon were incompletely resolved from those for the phenyl groups, and therefore an accurate determination of the shift tensor principal components was not obtained. Spectral overlap in the static spectrum also proved problematic; however, resolution was sufficient to ascertain that the tensor is approximately axially symmetric with a $\Delta\sigma$ of 25 ± 2 ppm.

Discussion

The form of the powder pattern observed for **1** is quite sensitive to the relative orientation of the ^{31}P dipolar tensor with respect to the chemical shift tensors, thus allowing a partial assignment of their relative orientation. In the general case of two coupled spin 1/2 nuclei both chemical shift tensors, the indirect and direct dipolar tensors and the Euler angles relating these tensors to a common frame are required for a full description of the spectrum. The powder pattern alone is insufficient to determine uniquely all 18 of these parameters, and some must be determined independently if a unique result is to be obtained. Of prime importance is the classification of the two spin system as AX, AB, or A_2 . For solid state spectra this requires one to consider all orientations of the molecule with respect to the magnetic field as both the chemical shift differences and dipolar couplings are orientation dependent. In the absence of isotropic tumbling, solution systems that are A_2 can become AB at many orientations in the solid.²⁵

Some help with the assignment here is given by the MAS spectrum of **1** (Figure 1A). This spectrum provides two important

pieces of information. First, the isotropic shift, which is the average of the three chemical shift tensor components, is independently determined and is the same for both ^{31}P centers. Secondly, the narrow line width indicates that the chemical shift for both nuclei must be close to the same at all orientations, i.e., the principal axes for the two shift tensors must be very close to parallel and thus the two ^{31}P nuclei form an A_2 system. This follows from considering how MAS affects solid state A_2 or AX spin systems differently than AB spin systems. For a dipolar coupled pair of spin 1/2 nuclei the line shape behaves inhomogeneously if the chemical shift difference between the two nuclei is (1) much larger than their mutual dipolar coupling at all orientations or (2) close to zero at all orientations. Thus in the A_2 or AX cases MAS will produce sideband spectra with narrow lines at all spin rates just as in the case of a single spin 1/2 nucleus with a chemical shift anisotropy.^{19,20} For AB systems, where the dipolar couplings and chemical shift differences are similar at most orientations, the line shape behaves more homogeneously and MAS gives a different result. In this case MAS does not usually produce resolved sidebands until the spin rate is comparable to the dipolar couplings and the line widths are a function of the spin rate.¹⁹ This can easily be appreciated by noting that the wave functions describing the spin system are different at the successive orientations passed through in the MAS cycle for the AB case,²⁴ whereas in the AX or A_2 cases the wave functions remain the same at all times in the MAS rotation. These effects can also be understood from the viewpoint of average Hamiltonian theory.¹⁹

Comparison of the MAS line widths for compounds **1-3** supports the assignment of **1** as an A_2 system by using the above criteria. In the case of the diphosphine **2** the shift tensors are expected to be far from colinear if the preference this compound has for the anti conformation³¹ is satisfied in the solid. Thus this spectrum should be characteristic of an AB system under MAS. In fact the line widths of 360 Hz observed for **2** is much wider than the 65 Hz measured for the single ^{31}P nucleus in **3**. The MAS spectrum for **1** displays just as narrow a resonance as **3** indicating that there is little, if any, AB character in this spin system.

With a known value for the isotropic shift and the assumption that the spin system can be classified as A_2 , the number of unknown is now reduced to 11. These are the strength of the dipolar coupling, the polar angles that relate the P=P internuclear vector to the CSA principal axis system, two shift tensor components, the anisotropic part of the ^{31}P - ^{31}P J coupling, and the Euler angles that relate the J coupling tensor to the CSA tensor. The combined direct and indirect dipolar interaction is determined independently by the 2D spectrum (Figure 2). Since the indirect and direct dipolar interactions involve the same spin operators, they cannot be easily separated, especially without single-crystal NMR and X-ray data.¹⁹ The Pake doublet pattern shown in Figure 2 is therefore the result of the combination of the direct and indirect dipolar tensors. If the indirect and direct dipolar tensors are not colinear, then the resultant tensor may depart from axial symmetry. In addition, the indirect dipolar tensor is not restricted by symmetry to be axially symmetric as in the case of the direct dipolar interaction. However, the main peaks of the observed Pake pattern are fairly well defined and do not exhibit any significant departure from axial symmetry. This is taken as evidence for the colinearity of the indirect and direct dipolar tensors and for the approximate axial symmetry of the indirect dipolar tensor. In the AB case the results of these experiments are expected to be more complicated as the chemical shift effects will not be fully removed in the spin echo. Three Pake patterns with complex intensities are expected in an AB system²¹ and this is not observed in the 2D spectrum for **1**. In addition, the echo modulation results are less sensitive to AB effects and would give different results than the 2D experiment if this were the case. The apparent axial symmetry of the combined indirect and direct dipolar tensors also suggests that the unique axis of this tensor lies along the P=P vector, providing an internal reference to the molecular frame.

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Since **1** is essentially an A_2 spin system, only the anisotropy of the J tensor is observed. The splitting in this pattern is the result of an effective $D' = D + (J_{11} - J_{33})/3$ and is measured as 2800 ± 100 Hz. By using the known bond length⁴ of 2.034 Å in $D = \gamma^2 h^2 / 4\pi^2 r^3$ a value for D of 2340 Hz is calculated. Since the sign of the coupling D' is not determined experimentally, this gives two possibilities for $\delta = J_{33} - J$, -920 Hz or +10 280 Hz. A few other ^{31}P scalar anisotropies have also been reported previously,^{24,27} unfortunately any interpretation of these data would be idle speculation until the signs of these anisotropies can be determined by theory²⁹ or very low-temperature experiments.

By using the 2D data the full powder line shape was simulated to determine the principal values of the shielding tensor and the orientation of the P=P vector in the CSA principal axis system. The result is shown in Figure 1C where the CSA values were found to be $\sigma_{11} = 1236$, $\sigma_{22} = 249$, and $\sigma_{33} = -3$ ppm with an estimated error of ± 4 ppm. The calculated line shape is quite sensitive to the orientation of the dipolar tensor in the chemical shift tensor axis system and to the value of D' . A best fit places the P=P vector perpendicular to the direction of σ_{33} and 30° from σ_{22} in a plane containing both σ_{22} and σ_{11} . The coincidence of the two discontinuities at the low field end of the spectrum and the separation between the breaks at the high field end could only be fitted with the inclusion of the J anisotropy and the twist angle of 30° . Attempts to fit the spectra by using the calculated value of D and ignoring the anisotropy in J were unsuccessful, further supporting the interpretation of the spin echo results.

This assignment still does not completely determine the shift tensor orientation in the molecular frame as any rotation of both shift tensors about the P=P vector is compatible with the spectrum. For further interpretation the absolute orientation of the shift tensor with respect to the molecular coordinates must be known. In ethylene the tensor orientation has been assigned^{24a} on the basis of dipolar spectra, symmetry, and previous single-crystal studies on olefins.^{24b} The orientation found places the most upfield component perpendicular to the molecular plane and the most downfield component in this plane and perpendicular to the C=C bond. The tensor orientation in tetramesityldisilene (**4**) is unknown and has been assigned in analogy to that found in ethylene, although the Si=Si moiety does not strictly conform to a planar geometry. In a calculation described below, the highest field component for the P=P double bond is also found to be approximately perpendicular to the CPP plane in analogy to ethylene. Since the CPP moiety in **1** deviates from planarity⁴ by about 8° this would have been expected to cause the shift tensors for the phosphorus centers to not be colinear. Simulations in which the shift tensor axes were rotated by 8° from one another did not match the experimental spectrum as well as when they were constrained to be parallel. This observation leads us to conclude that the σ_{33} component is probably close to being perpendicular to a plane containing the P=P bond with the aryl groups disposed equally above or below the plane.

Given the orientation of σ_{33} in **1** as described above, we now turn to the placement of the other two shielding components in the approximate CPPC plane. As discussed above, the powder spectrum of **1** is only consistent with σ_{22} being 30° away from the direction of the P=P vector in this plane. This is basically the same ordering observed in ethylene but is a significant deviation from having σ_{22} strictly along the double bond axis. The spectra do not determine whether the rotation of σ_{22} away from the P=P vector is toward the aryl group or the lone pair. To answer this question we resort to comparison with quantum mechanical calculations of the shielding tensor in 1,2-dimethyldiphosphine. As mentioned earlier the results place σ_{33} perpendicular to the CPPC plane. The calculation also places σ_{22} 18.7° off the P=P axis in the direction toward the phosphorus lone pair. In terms of absolute shielding the values obtained are $\sigma_{11} = 1272$, $\sigma_{22} = -422$, and $\sigma_{33} = -850$ ppm relative to the isotropic shift which was calculated as 321 ppm with respect to a bare ^{31}P nucleus. The calculated values for the chemical shift tensor elements do not reproduce the observed parameters very well as might be expected given that methyl groups have been used in place of 2,4,6-tri-

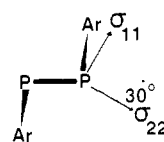


Figure 4. Schematic representation of the orientation of the chemical shielding tensor in **1**. The σ_{22} component lies approximately along the lone pair in this plane. The highest field component σ_{33} is perpendicular to the plane depicted and the 2,4,6-tri-*tert*-butylphenyl groups are disposed slightly below or above this plane.

tert-butylphenyl groups. Past experience with calculations of ^{13}C chemical shift tensors indicates that the orientation of the tensor in the molecular axis system is accurately derived^{12,32} much more easily than the actual values of the components themselves. Furthermore it has been observed in alkenes that substituent effects generally manifest themselves in changes in the size of the principal components of the shift tensor and do not result in any change in the ordering of the components. Therefore, since the ordering and orientation are approximately those found experimentally, the agreement is taken as sufficient to be certain of the assignment of σ_{22} as being directed toward the lone pair.

The overall view arrived at in this study is that the high field component of the chemical shift tensor in **1**, is perpendicular to the approximate CPPC plane and the intermediate component is 30° off of the P=P bond in the direction away from the aryl group. The low field component is then approximately perpendicular to the lone pair (Figure 4). While the data presented here are well accounted for by this description, it is difficult to estimate the uncertainties in these parameters for a variety of reasons. First the deviation of the CPPC moiety from planarity is not fully consistent with the assignment of the spin system as A_2 . In addition, it is well known that the orientation of a shift tensor's principal axis system does not necessarily coincide with the axis dictated by the symmetry of an isolated molecule. Single-crystal studies have shown that this can be quite sensitive to any lowering of the molecular symmetry due to crystal packing. Thus while the spectra are consistent with the A_2 description, some small deviation from this condition is probably acceptable. The quality of the 2D data is also not sufficient to totally rule out any nonaxially symmetric character in the dipolar interaction and thus the assumption that the indirect dipolar tensor is axially symmetric and has its unique axis directed along the P=P vector is not rigorous. All of these small factors could conceivably tend to cancel one another out and still give a spectrum consistent with the proposed model. On the other hand, the agreement of the experimental spectrum for **1** and that calculated under these assumptions is so good that deviations in the orientations of any of the tensors by more than 10° is very unlikely. For the purposes of comparison with other multiply bonded systems the parameters derived here are then perfectly adequate.

Comparison to Group 14 Double Bonds. The spectra presented here make a striking comparison with those of Figure 1 in ref 14. For compound **1** the span of the CSA is observed to be an order of magnitude larger than in the singly bonded analogue in accordance with the previous observations for ^{13}C and ^{29}Si in similar systems. A measure of the relative increase in the anisotropy of the electronic structure in the doubly bonded species over their singly bonded counterparts can be obtained by comparing their values of $\Delta\sigma = |\sigma_{11} - \sigma_{33}|$. Such comparisons however should be done cautiously as the $\Delta\sigma$'s for sp^3 carbons are known to vary much more relative to one another than those for sp^2 carbons do. For a series of 10 simple alkenes¹³ the $\Delta\sigma$ values cover a range of 195–234 ppm which is only a $\pm 9\%$ variation from the average $\Delta\sigma$. On the other hand, in a similar set of hydrocarbons, methylenes^{12b} and methylenes^{12c} are observed to have $\Delta\sigma$'s ranging from 4–36 and 16–99 ppm, respectively. Since the range of observed $\Delta\sigma$'s is as large or larger than the $\Delta\sigma$'s themselves, some caution must be exercised in the choice of the singly bonded compound

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Table I. Comparison of Tensor Elements^f

type	observed				scaled ^a			
	σ_{11}	σ_{22}	σ_{33}	$\Delta\sigma$	σ_{11}	σ_{22}	σ_{33}	$\Delta\sigma$
C=C ^b	234	120	24	210	234	120	24	210
Si=Si ^c	180	27	-15	195	271	104	59	212
P=P ^d	1236	249	-3	1239	359	120	58	301
C—C ^{e,h}	(28)	(28)	(4)	25	(28)	(28)	(4)	25
Si—Si ^f	-37	-56	-72	35	35	14	-3	38
P—P ^{g,h}	(-27)	(-27)	(-117)	90	(52)	(52)	(30)	22

^a Scaled by using either $\delta^{13}\text{C} = 0.243 \delta^{31}\text{P} + 59$ or $\delta^{13}\text{C} = 1.09 \delta^{29}\text{Si} + 75$. ^b Ethylene. ^c Compound 4. ^d Compound 1. ^e 1,1,2,2-Tetraphenylethane. ^f Compound 5. ^g Compound 2. ^h (σ) calculated assuming axial symmetry by using the isotropic shift and the observed $\Delta\sigma$. ⁱ All ¹³C and ²⁹Si shifts in ppm referenced to TMS. ^j ³¹P shifts in ppm referenced to 85% orthophosphoric acid. Scaled shifts are also on the ¹³C shift scale in ppm referenced to TMS.

that is to be compared with the doubly bonded species. Qualitatively this is easy to understand. Small shifts in tensor components due to substituent effects or sterics will produce larger percentage changes in the $\Delta\sigma$ values observed for alkanes than for alkenes which are dominated by the sp^2 hybridization. In methylenes even the ordering of the tensor components in the frame dictated by the local symmetry can change as discussed by Facelli et al.^{12c} Thus a median $\Delta\sigma$ value, such as the 25 ppm measured for the methine in 1,1,2,2-tetraphenylethane, is a more fair comparison to alkenes than the smaller value observed for ethane for our present purposes. For carbon the ratio of $\Delta\sigma$'s for C=C to C—C bonds is then about 8. This compares favorably to the ratio of ³¹P $\Delta\sigma$ values found for 1 and 2 in the present work of about 13. In the ²⁹Si spectra of tetramesityldisilene (4) and tetramesityldisilane (5), the patterns differ by a factor of 5 in width. Given that the $\Delta\sigma$ values for ³¹P in diphosphines and ²⁹Si in disilanes are likely to be as variable as those found for ¹³C in alkanes, additional data are needed to further interpret these differences (vide infra). Nevertheless the results indicate that there is a gross similarity between the electronic structure in these three types of double bonds.

It is interesting to note that the position of σ_{33} in the three doubly bonded species being compared all fall slightly to the low field side of their singly bonded counterparts spectra. This indicates that there is indeed a great deal of similarity in the electronic structure of the σ bonding system that this shielding component samples in all three compounds. In the phosphorus case σ_{33} should be sensitive to the presence of the lone pair which evidently has a rather similar effect on this component in both diphosphines and diphosphines.

Given the difficulties in comparing $\Delta\sigma$ values, it is tempting to directly compare the magnitude of the anisotropies observed for ethylene, 1, and 4. However, unless the intrinsic changes associated with moving from ¹³C to ²⁹Si to ³¹P are factored out first, little is to be learned about the differences in their electronic structures. Early work by Jameson and Gutowsky³³ demonstrated that the ranges of isotropic shifts observed for nuclei heavier than hydrogen could be explained by considering only the paramagnetic term, σ_p , and considering the diamagnetic term to be roughly constant for any particular isotope. In their work σ_p was shown to be proportional to the product of $\langle 1/r^3 \rangle$, the mean inverse cube radius of the non-s electrons, $1/\Delta E$, the inverse of the average excitation energy, and a third factor related to the nature of the bonding. The latter two terms cause the familiar variation in shift accompanying changes in chemical environment for a particular nucleus. This range is scaled by the $\langle 1/r^3 \rangle$ term which has an intrinsic periodic dependence on the atomic number Z. Although simple, this theory successfully predicts the observed Z dependence of chemical shift ranges. In addition it also accounts for the linear correlations found between chemical shifts for different nuclei³⁴ in series of isoelectronic and isosteric compounds, i.e., ¹³C shifts in alkanes and ²⁹Si shifts in silanes with similar structures. The slopes in these correlations generally agree with the ratio of the

values of $\langle 1/r^3 \rangle$ calculated in Jameson and Gutowsky's work³³ for the appropriate nuclei. For comparison some representative examples of $\delta X/\delta Y$ calculated (observed) are $\delta^{119}\text{Sn}/\delta^{29}\text{Si} = 4.5$ (5.12),^{34a} $\delta^{15}\text{N}/\delta^{13}\text{C} = 2.5$ (2.05),^{34b} $\delta^{11}\text{C}/\delta^{11}\text{B} = 1.6$ (1.71),^{34c} $\delta^{207}\text{Pb}/\delta^{119}\text{Sn} = 1.9$ (2.42),^{34a} and $\delta^{29}\text{Si}/\delta^{13}\text{C} = 2.0$ (0.95).^{34a} With the exception of the value for $\delta^{29}\text{Si}/\delta^{13}\text{C}$, the values arrived at with this level of theory compare quite well to those found experimentally. In the latter case^{34a} the Si d-orbitals were included in the calculation. Better agreement would be expected if only p-orbitals were included in the calculation and at the SCF level³⁵ a value of 1.2 is arrived at which is indeed much closer to the observed slope.

The now extensive body of experimental and theoretical studies of ¹³C chemical shift tensors supports the notion that variations in the tensor components can also be most easily understood by considering only the paramagnetic term.¹¹⁻¹³ In view of the above observations on isotropic chemical shifts, a rational way to compare tensorial shifts for different nuclei would be to scale them according to the linear correlations found between their isotropic shifts. At present no correlation between ³¹P shifts and either ¹³C or ²⁹Si shifts has been published to our knowledge. To aid us in this comparison a cursory sample of ¹³C shifts^{11-13,36-38} in alkanes, alkenes, alkynes, allenes, ketenes, and cyclopropanes without any heteroatom substituents have been compared to their trivalent phosphorus containing analogues^{37,38} giving a slope $\delta^{31}\text{P}/\delta^{13}\text{C}$ of 4.1 which compares favorably to the value of 3.25 predicted by Jameson and Gutowsky's work. With use of the appropriate experimentally determined isotropic chemical shift correlations, the tensorial shifts for the compounds being compared have been converted to the ¹³C shift scale, and the results are shown in Table I.

At first glance the scaled results for the C=C, Si=Si, and P=P bonds compare quite well. The σ_{22} components are close to one another as are the values for σ_{33} . While the σ_{11} values for ¹³C and ²⁹Si are comparable, that for ³¹P in 1 is still significantly larger, and the $\Delta\sigma$ is about a factor of 1.5 larger on this scale. It is interesting to note that the σ_{11} component in the diphosphene is approximately perpendicular to both the lone pair and the phosphorus p_z orbital involved in the π bond. This component then should be the most sensitive to any low lying transition such as $n \rightarrow \pi^*$ involving the lone pair, and the low field shift observed may be caused by the smaller excitation energy for such a transition.

The present comparisons should however be made cautiously as they are not strictly addressed by the current theory. The

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experimentally determined shift correlations used here hold only if one center at a time is replaced by the main group element even though this means that polar and nonpolar bonds are being compared. The fact that the observed isotropic shift correlations are so good indicates that bond polarity must only affect these correlations in a constant additive or multiplicative manner. Therefore ^{13}C alkene shifts should be compared to ^{29}Si silene and ^{31}P phosphalkene chemical shifts. The ^{29}Si shifts for the disilene **4** and the ^{31}P shifts for the diphosphene **1** should also be compared to ^{13}C tensors in silenes and phosphalkenes, respectively. These data are not currently available; however, isotropic shifts^{24,37,38} for these species are available. If the isotropic shifts and $\Delta\sigma$ values in general follow the same correlations, then the data indicate that ^{13}C $\Delta\sigma$'s in silenes and phosphalkenes should be expected to be significantly larger than in olefins. Likewise the ^{31}P $\Delta\sigma$'s in phosphalkenes are expected to be smaller than the $\Delta\sigma$ reported here for the diphosphene **1**. Another factor to consider in these comparisons is that **1** is far from being isostructural with alkenes as the PCC angle is close to 103° rather than 120° . Further study is required to determine the effect that this change in geometry has on chemical shifts. In a similar vein, while the results for the disilene compare quite well to ethylene when scaled, this agreement may be fortuitous as **4** is not strictly planar.

The results for the singly bonded species can be discussed in a similar fashion. However, this is not expected to be as informative as exercise as in the case of the multiply bonded species for reasons discussed previously. The competing factors determining these shifts place a much greater importance on the requirement that chemical shifts only be compared for different nuclei in isostructural species, and this condition is not satisfied for the present data.

Conclusions

Even though there is a significant twist of the shift tensor orientation in **1** about σ_{33} , the overall comparison to the Si=Si and C=C bonds is good especially when the intrinsic change in chemical shift upon substitution of another main group element

for carbon is accounted for. This is in parallel with the observation that ^{13}C shift tensors in unsymmetrically substituted alkenes are quite similar to that in ethylene. While the σ_{22} components in ethylene, **1**, and **4** do not lie along the same axis, they still match well in magnitude when scaled. The size of the CSA in **1** is about 6 times that found in ethylene or **4**, but much of this is a reflection of the fact that ^{31}P shift anisotropies for trivalent phosphorus tend to be larger than ^{13}C or ^{29}Si CSAs for all types of bonding. When this is accounted for the difference is only about a factor of 1.5. This larger $\Delta\sigma$ is primarily due to the extreme low field position of σ_{11} in **1**. The orientation of σ_{11} reported here suggests that the origin of this additional paramagnetic shift may be the existence of a low-lying transition such as $n \rightarrow \pi^*$ involving the phosphorus lone pair and the π bond. Before further conclusions can be drawn, studies of the shielding in phosphalkenes and silenes are needed. A theoretical treatment of the effects that the differences in the geometry of these species have on chemical shifts would also be helpful.

In conclusion this work provides a good experimental foundation on which the electronic structure of diphosphenes can be compared to disilenes and olefins. The shift tensor reported in this work will also prove to be a good test for the accuracy of wave functions used in quantum mechanical investigations of P=P bonds. Further work is in progress to test the generality of the method used here to compare shift tensors for different elements and the predictions of unknown shift tensors based on it.

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