noise-free data, essentially exact solutions are obtained when $\tau_c t_m$ < 1.5 × 10^{-9} s^2. In contrast, the accuracy of d_{ij} values obtained by using a two-spin approximation is not increased by improvements in the data because of the inherent error in neglecting multispin relaxation effects.

Procedures involving a matrix analysis are being actively investigated. Although the requirement for nearly complete data with well-determined intensities may prohibit a multispin analysis of interproton distances in the first steps of structure determination by NMR, such an analysis is beneficial in refinement of the structural solution. The need for nearly complete NOESY data sets can be circumvented in the first stages of structure determination by combining experimental data with cross-peak intensities calculated from an initial model.[30,37,55,59] An iterative procedure could also serve to improve the quantification of NOESY intensities for instances such as overlapping resonances. Furthermore, a novel approach utilizing NOESY data directly

in the conformational search, in contrast to the interproton distances interpreted from them, was recently reported.[60] At the least, the final structure should be evaluated by comparing simulated NOESY cross-peak volumes calculated from the structural solution with the experimentally observed NOESY volumes, perhaps in a fashion analogous to the crystallographic *R*-factor[22,61,62] or as an average percent difference,[59] with some provision for possible discrepancies resulting from internal motions.

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Nature of the Carbon–Phosphorus Double Bond and the Carbon–Phosphorus Triple Bond As Studied by Solid-State NMR

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Abstract: The nature of the carbon–phosphorus double bond in 2,4,6-*t*-Bu$_3$C$_6$H$_2$P=C(SiMe$_3$)$_2$ and the carbon–phosphorus triple bond in 2,4,6-*t*-Bu$_3$C$_6$H$_2$C≡P has been studied by ^{13}C and ^{31}P solid-state NMR. Magic angle spinning and static cross-polarization experiments have been used to determine the principal elements of the ^{13}C and ^{31}P shielding tensors. In the ^{13}C spectra, the presence of a dipolar coupling to the ^{31}P nucleus permits assignment of the orientation of the ^{13}C shielding tensors in the molecular frame. These shift tensors are compared to previous work on diphosphenes, disilenes, alkenes, and alkynes. It is found that the shift anisotropies for ^{31}P and ^{13}C in these multiply bonded environments are quite similar when the larger intrinsic chemical shift range for ^{31}P is taken into account.

Introduction

Advances in synthetic chemistry over the last two decades have resulted in the successful synthesis and isolation of a variety of main-group compounds containing multiply bonded functional groups.[2] Examples of room temperature stable species with Si=Si,[3] P=P,[4] and Sn=Sn[5] double bonds have been realized, as well as compounds with multiple bonds between main-group and transition elements. A number of mixed-main-group systems with, e.g., C=Si,[6] C=P,[7] and C≡P[7] multiple bonds are also now

known. In this paper we report the first use of solid-state NMR methods to investigate the nature of the C=P double bond in 2-(2,4,6-tri-*tert*-butylphenyl)-1,1-bis(trimethylsilyl)phosphaethene (1) and the C≡P triple bond in 2-(2,4,6-tri-*tert*-butylphenyl)-phosphaacetylene (2). Previous efforts to characterize these novel compounds have involved studies of their chemical reactivity or used structural methods in addition to theoretical treatments. Reactivity of 1, 2, and related compounds has been found to compare favorably with that of similar alkenes and alkynes.[7,8] X-ray crystallography finds the C=P bond length in 1 to be 1.665

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Å[9a] and the C≡P bond length in **2** to be 1.516 Å.[9b] This ~9% shortening of the carbon-phosphorus bond upon going from a C=P bond to a C≡P bond parallels the 10% bond contraction on going from ethylene to acetylene. These structural trends are mirrored by ab initio calculations that have also been used to predict bond strengths, electronic properties, and other structural features of the parent systems or other model compounds.[10] In addition, similarities in the NMR chemical shift trends from solution studies have been pointed out as evidence for similarity in the bonding in these molecules and their wholly organic counterparts.[8d]

The anisotropy of the chemical shift has been well-established as a sensitive measure of the three-dimensional electronic structure surrounding an NMR-active nucleus. Previously, this group has used solid-state NMR in combination with quantum mechanical calculations to characterize the P=P bond and to compare it with double bonds among other group IV elements.[11] In that work, the anisotropic ^{31}P chemical shifts for the P=P bond were found to correlate quite well with the ^{13}C shifts in alkenes and the ^{29}Si shifts in disilenes when the larger intrinsic shift range for phosphorus was taken into account. In the present paper these correlations are extended to compounds containing C=P and C≡P bonds. The trends in ^{31}P tensorial shifts are found to follow those for ^{13}C in analogous organic systems. It was predicted in our earlier work that the anisotropy of the chemical shift for ^{13}C in the C=P bond should be larger on an absolute scale than those in alkenes, and that the ^{31}P shift anisotropy should be smaller than in a diphosphene.[11] This has indeed turned out to be the case.

Theory

Comparison of Chemical Shifts. In order to derive any insight into the bonding in these multiply bonded species from the shielding anisotropies, one must have a method for comparing chemical shifts for different nuclei. It has been known for some time that the isotropic chemical shifts for pairs of nuclei in isostructural molecules will fall on a straight line when plotted versus one another.[12] For example, consider pairs of molecules in which a C-H fragment is replaced by N: e.g., methane and ammonia or benzene and pyridine. When the ^{13}C shifts are plotted versus the ^{15}N shifts for the centers in question, it is experimentally found that they are linearly correlated.[13a] This observation is usually explained by noting that the variations in isotropic chemical shifts are often dominated by the local paramagnetic shielding term σ_p. In Pople's approximate LCAO-MO theory of chemical shielding,[14] the zz component of σ_p is given by

$$\sigma_p^{zz} = -\frac{e^2\hbar^2}{2m^2c^2(\Delta E)}\langle r^{-3}\rangle_{np,nd}\{(Q_{AA})_{zz} + \sum_{B\neq A}(Q_{AB})_{zz}\} \quad (1)$$

where

$$(Q_{AA})_{zz} = 2 - 2(P_{x_Ax_A} - 1)(P_{y_Ay_A} - 1) + 2P_{x_Ay_A}^2$$

and

$$(Q_{AB})_{zz} = -2P_{x_Ax_B}P_{y_Ay_B} + 2P_{x_Ay_B}P_{y_Ax_B}$$

The $P_{\mu\nu}$ are elements of the charge density bond order matrix of

the unperturbed molecule, and ΔE is an average electronic excitation energy. For a given bonding arrangement, the $(Q_{\alpha\beta})_{zz}$ terms will largely be the same. If the excitation energy is relatively constant, σ_p is then proportional to the inverse cube of the radial displacement of the p or d valence electrons, $\langle 1/r^3\rangle_{np,nd}$, involved in the shielding of the nucleus under consideration. Therefore, the slope of one of these chemical shift correlation plots can be rationalized to be the order of the ratio of the $\langle 1/r^3\rangle_{np,nd}$ factors for the two nuclei involved. The slopes experimentally observed in isotropic shift correlations are in fact often quite close to such values. Examples of shift correlation slopes calculated in this way as $\delta(X)/\delta(Y)$ = calculated (observed) are $\delta(^{119}Sn)/\delta(^{29}Si)$ = 4.5 (5.12),[13b] $\delta(^{29}Si)/\delta(^{13}C)$ = 2.0 (0.95),[13b] $\delta(^{207}Pb)/\delta(^{119}Sn)$ = 1.9 (2.42),[13b] $\delta(^{13}C)/\delta(^{11}B)$ = 1.6 (1.71),[13c] and $\delta(^{15}N)/\delta(^{13}C)$ = 2.5 (2.05).[13a] As first pointed out by Jameson and Gutowsky, the variation in $\langle 1/r^3\rangle_{np,nd}$ from element to element explains the periodic variation or Z dependence in the size of the chemical shift ranges for different nuclei for the same reason.[15]

The $\langle 1/r^3\rangle_{np,nd}$ dependence of the chemical shift is in fact more deeply rooted in the physics of the shielding phenomenon than the above discussion would indicate. Whether the shielding equations are cast in Ramsey's form,[16a] in terms of current densities,[16b] or in the LORG formalism,[16c] one notes that all pertinent terms contain $1/r^3$ denominators. Thus, the entire chemical shielding should be proportional to $\langle 1/r^3\rangle_{np,nd}$, regardless of the partitioning into paramagnetic and diamagnetic terms. Perhaps the most straightforward way in which this can be appreciated is to consider the chemical shift in terms of the field experienced by the nucleus due to the surrounding electrons following Flygare's treatment.[17] The net field $\vec{H}_e^k$ at the kth nucleus due to the motion of the ith electron in a molecule can be written as

$$\vec{H}_e^k = -\frac{e}{c}\sum_i\frac{\vec{r}_{ki}\times\vec{v}_{ki}}{|\vec{r}_{ki}|^3} \quad (2)$$

where $\vec{r}_{ki}$ is the vector from the kth nucleus to the ith electron with velocity vector $\vec{v}_{ki}$.[17] That the field $\vec{H}_e^k$, i.e., the chemical shift, should depend on the value of $\langle 1/r^3\rangle_{np,nd}$ may simply be a consequence of the denominator in eq 2.

Regardless of any theoretical justification, such isotropic shift correlations are an empirical observation and can serve as a basis for comparison of chemical shifts in isostructural pairs of molecules differing by replacement of one nucleus for another. For the purpose of this paper, an isotropic chemical shift correlation for ^{13}C and ^{31}P shifts[11,18] will be applied in a similar fashion to the *anisotropic* chemical shifts. Thus, the relation

$$\delta(^{13}C) = 0.261\delta(^{31}P) + 59 \quad (3)$$

will be used to compare ^{13}C shift tensor elements measured with respect to TMS to ^{31}P shifts referenced to 85% H_3PO_4. When ^{13}C and ^{31}P shifts compare well by use of eq 3 to remove the intrinsic Z dependence, similarity in the bonding arrangement, i.e., terms such as the $(Q_{\alpha\beta})_{zz}$'s, is implied. Further implications of this type of shift correlation between the anisotropic chemical shifts of several nuclei will be dealt with in another paper.[19]

Effect of Dipolar Couplings. The solid-state spectra for the ^{13}C adjacent to the phosphorus centers in **1** and **2**, in addition to being affected by the CSA, will have a contribution due to the direct dipolar and indirect dipolar or J couplings.[20] The powder spectrum in this case is an overlapping pair of CSA powder patterns, one of which is stretched by the dipolar coupling and the other of which is contracted. The discontinuities in this pattern can be shown[20] to appear at the principal values of the two tensors T^+ and T^- related to the chemical shift tensor ν (written in fre-

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Table I. Chemical Shielding Tensors and Dipolar Couplings[a]

| compd | nucleus | chemical shift | | | | J | D_T | ΔJ |
		σ_{11}	σ_{22}	σ_{33}	σ_{iso}			
1	^{31}P	819	249	-31	394			
1	$^{13}C{=}P$	379	151	44	191	91	2390	-777
								-15117
1[b]	$^{13}C{-}P$	242	107	83	144	90	1605	-1008
								-10638
2	^{31}P	229	140	-274	31			
2	$^{13}C{\equiv}P$	290	290	-60	169	59	3098	-1233
								-19821

[a] ^{31}P shifts (ppm) referenced to 85% orthophosphoric acid. ^{13}C shifts (ppm) referenced to TMS. Shifts reported taking downfield as positive, and all couplings are reported in hertz. J, D_T, and ΔJ are defined in the text. [b] Aryl carbon bonded to phosphorus.

quency units), the direct dipolar tensor **D**, and the indirect dipolar tensor **J** by

$$\mathbf{T}^{\pm} = \mathbf{R}\cdot[\nu \pm \tfrac{1}{2}(\mathbf{R}'\cdot\mathbf{D}\cdot\mathbf{R}'^T + \mathbf{R}''\cdot\mathbf{J}\cdot\mathbf{R}''^T)]\cdot\mathbf{R}^T \qquad (4)$$

In eq 4, $\mathbf{R}'$ and its transpose rotate the direct dipolar tensor into the principal axis of ν. The rotation matrix $\mathbf{R}''$ performs this transformation for the indirect dipolar tensor **J** and the rotation matrix **R** diagonalizes the net result of the three terms. **D** is taken as having its z axis along the carbon-phosphorus bond and has elements $D_{xx} = D_{yy} = D$ and $D_{zz} = -2D$ in its principal axis system. The dipolar coupling constant D is given in frequency units by

$$D = \frac{\gamma^C\gamma^P\hbar}{2\pi r_{CP}^3} \qquad (5)$$

In eq 5, γ^C and γ^P are the gyromagnetic ratios for carbon and phosphorus, and r_{CP} is the effective carbon-phosphorus internuclear distance after vibrational averaging has been taken into account. When magic angle spinning (MAS) is used, the halves of the chemical shift anisotropy broadened dipolar doublet behave as individual effective chemical shift tensors with each breaking into a spinning sideband pattern. The sideband intensities can be calculated by use of the method of Herzfeld and Berger[21] for the tensors $\mathbf{T}^+$ and $\mathbf{T}^-$. In the MAS spectrum these patterns appear separated by the isotropic scalar coupling J.[22]

The six discontinuities in the powder spectra can uniquely determine only six of the twelve parameters implied in eq 4. It will be assumed in what follows that the direct and indirect dipolar tensors have the same principal axis system. Furthermore, it will be assumed that the indirect dipolar tensor is axially symmetric. The net dipolar interaction then is parameterized by an effective total dipolar coupling $D_T = D + (J_\perp - J_\parallel)/3$. In cases where the sum of the direct and indirect dipolar tensors have been measured between pairs of ^{31}P nuclei using single-crystal rotation patterns, these assumptions are found to be valid.[23] This leaves seven parameters to be determined: the three principal elements of the chemical shift tensor, D_T, the isotropic J, and the two polar angles giving the orientation of the z axis of the total dipolar tensor in the chemical shift tensor principal axis system. The isotropic J and the average of the three principal components of the chemical shift can be determined independently from the MAS spectrum. Therefore, the unknowns are overdetermined by one observable within the limitations of these assumptions. Since **J** and **D** have the same form, they cannot be separated by these NMR experiments. To estimate the difference $J_\perp - J_\parallel = \Delta J$, a value for r_{CP} must be known from an independent source so that D can be calculated.[23] One is still left with an ambiguity as to the sign of ΔJ.

Experimental Section

Compounds **1** and **2** were synthesized as described elsewhere.[9,24] Compound **1** was kept in a sealed 4-cm-long 5-mm-diameter glass tube, and compound **2** was stored in an unsealed 5-mm-diameter glass tube.

Neither sample was observed to change visually or by CPMAS NMR when stored in this manner over a period of 1 year.

NMR experiments were carried out at fields of 2.34 and 7.05 T with home-built spectrometers and probes.[11,25] The MAS turbine is designed to spin the sealed 5-mm tubes used for sample cells at rates of up to 3 kHz. Sealed sample cells were necessary for **1** due to its sensitivity to the atmosphere. Radio-frequency (rf) field amplitudes employed were typically 15, 36, and 60 G for ^1H, ^{31}P, and ^{13}C, respectively. Static ^{31}P NMR spectra have been obtained at both field strengths with cross polarization followed by a Hahn echo prior to data acquisition to avoid receiver recovery problems. CP mixing times were 2-3 ms, and the time τ between the CP step and the π pulse in the Hahn echo was 100-300 μs. Typical spectra required approximately 500 scans for ^{31}P, while 50000 were recorded for ^{13}C powder spectra. CPMAS spectra for ^{31}P and ^{13}C spectra were obtained at both fields with use of similar parameters. MAS spectra for ^{31}P are the result of approximately 100 scans, while those for ^{13}C required a few thousand. All ^{31}P spectra were externally referenced to 85% H_3PO_4, and ^{13}C spectra were externally referenced to TMS. Chemical shifts obtained in this manner are typically accurate to within ±0.5 ppm. Isotropic shifts in MAS spectra were determined by comparison of spectra taken at several spin rates.

Obtaining distortion-free ^{13}C powder spectra proved problematic at the higher field strength due to the extreme breadth of the patterns encountered and the large background signal from the associated ligands. Since the ^{13}C atoms bonded to ^{31}P atoms in **1** and **2** are at least three bonds away from the nearest proton, cross polarization is relatively inefficient. This leads to severe intensity distortions at off-resonance positions as the Hartmann-Hahn condition becomes progressively less well-matched. If the carrier was placed close to one set of discontinuities, the spectrum in that region was well-formed, while those at the other end of the pattern would be ill-defined. In order to accurately measure all of the pertinent spectral features, it was found that several spectra had to be acquired with the carrier frequency placed close to the spectral regions of interest.

Spectral simulations and other calculations were performed on an IBM PS/2 Model 80 microcomputer with SPCSIM, a powder and MAS simulation program, and FINDMR, a program that extracts CSA and dipolar tensor information from MAS sideband intensities by a least-squares numerical adaptation of the graphical method of Herzfeld and Berger.[21]

Results

The ^{31}P CPMAS spectra for compounds **1** and **2** are depicted in Figure 1. In both cases, only one ^{31}P site is indicated and the full width of the lines at half-maximum is ~30 Hz. Solid-state isotropic shifts are found to be 394 ppm for **1** and 31 ppm for **2**, which differ slightly from the solution shifts of 381 and 34 ppm reported previously.[9,24] The static ^{31}P NMR spectra shown in Figure 2 have well-resolved discontinuities at shifts corresponding to the three components of the shielding tensor. Simulations of these spectra yield the ^{31}P shift tensors reported in Table I. For both compounds, the spread of the anisotropic chemical shifts is quite large, ~850 ppm in the P=C double bond and ~503 ppm in the P≡C triple bond.

The ^{31}P spectra in Figure 2 show what appears to be noise riding on top of the powder patterns that is much larger than that in the baseline. This result has been determined not to be an experimental artifact, as it has been reproduced at both field strengths with different probe heads and different preamplifiers.

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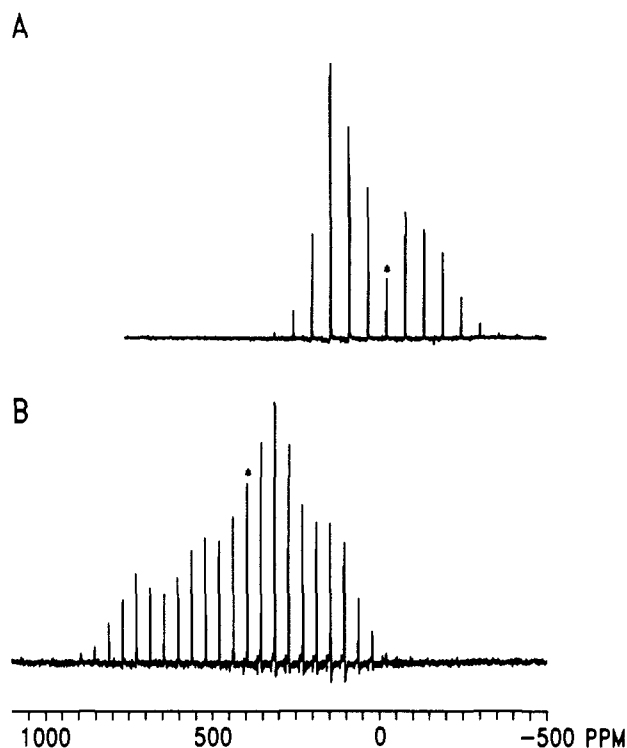
A

B

Figure 1. ^{31}P MAS spectra: (A) 2; (B) 1. Asterisk marks the isotropic shift. Zero on the shift scale corresponds to 85% H_3PO_4.

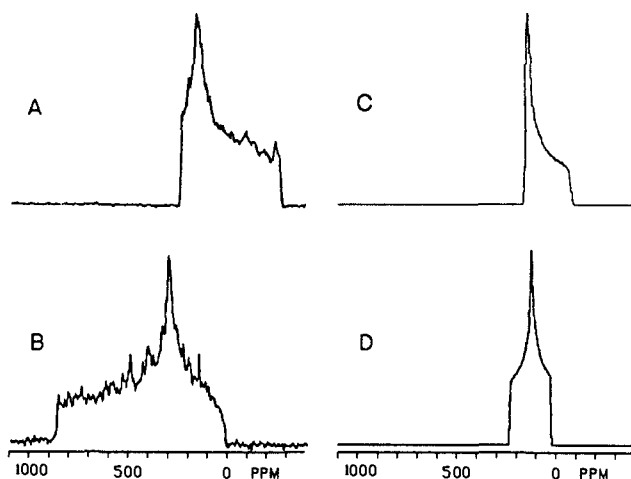**Figure 2.** ^{31}P powder spectra: (A) 2; (B) 1; (C) simulation for methylacetylene with parameters given in ref 27; (D) simulation for *trans*-2-butene with parameters given in ref 27. References: (A and B) 85% H_3PO_4; (C and D) TMS.

It is somewhat reduced by slow spinning of the samples at 10–100 Hz. Several cycles of regrinding and packing the sample of 2 were found to be ineffective in suppressing this effect.

^{13}C CPMAS spectra for compounds 1 and 2 are shown in Figure 3. Since the CSA-broadened dipolar doublets for the ^{13}C adjacent to the ^{31}P nuclei are much wider than the CSA patterns for the other carbon centers, the signals of interest are spread out over many more sidebands, making them difficult to observe. The solid-state isotropic chemical shifts in Table I are within a few parts per million of those observed in solution.[9,24] Isotropic ^{13}C–^{31}P J couplings in the solid are all found to be slightly greater than those observed in solution.[9,24]

The principal components of the T$^+$ and T$^-$ tensors for both the phosphaalkene carbon and the aryl carbon α the phoshorus in 1 were determined by analysis of the spinning sideband intensities. Because of the large breadth of the pattern for the phosphaalkene carbon, data from the 2.35-T instrument were used. For the aryl carbon, data at the higher field strength were used,
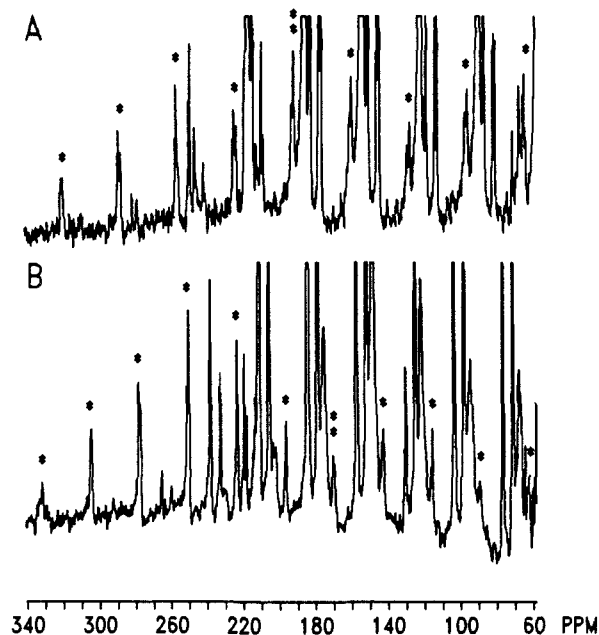

Figure 3. ^{13}C MAS spectra: (A) 1 (one asterisk indicates the sidebands, and two asterisks mark the isotropic shift for the carbon double-bonded to phosphorus); (B) 2 (one asterisk indicates the sidebands and two asterisks mark the isotropic shift for the carbon triple-bonded to phosphorus). Both A and B are referenced to TMS.

as the anisotropy in the chemical shift is significantly smaller. In both cases, the resulting T$^+$ and T$^-$ tensor components indicated that the total dipolar tensor was axially symmetric, consistent with the assumptions outlined earlier. The elements of the T$^+$ and T$^-$ tensors then determine the principal elements of the ^{13}C chemical shift tensors, the magnitude of the total dipolar coupling D_T, and the orientation of the carbon–phosphorus internuclear vector in the shielding tensor principal axis system. The components of the two ^{13}C shift tensors obtained in this way for 1 are listed in Table I. For the phosphaalkene carbon, the only orientation of the shift tensor that gives a satisfactory fit to the experimental data places the C=P bond along the σ_{22} component. For the aryl carbon, the σ_{11} component is found to lie along the C–P single bond. In either case, deviations by as little as 10° from these relative tensor orientations would produce spectra significantly different from those observed experimentally.

Attempts to derive tensor components from the spinning sideband patterns for the phosphaalkyne carbon in 2 failed to produce useful results with data from either field strength. This is partially a result of the fact that the T$^+$ and T$^-$ tensors in this case are very close to being axially symmetric. Several groups have previously noted[26] that it is difficult to reliably extract tensor components from sideband intensities for axially symmetric tensors, as sideband patterns are quite insensitive to variations in the asymmetry parameter η when it is less than 0.2. For this reason, the tensor components were extracted from powder spectra. Although the static ^{13}C spectrum for 2 contains sixteen overlapping resonances, three of the six possible T$^+$ and T$^-$ tensor components for the phosphaalkyne carbon can be observed, as the powder spectrum extends out from both sides of the other interfering powder patterns. The components observed along with the isotropic shift are sufficient to determine that the shift tensor is axially symmetric. The unique high-field component resonates at −60 ppm and is oriented along the C≡P bond.

The magnitudes of the total dipolar tensors, $D + (J_\perp - J_\parallel)/3$, derived from the above fits for both molecules, are also included in Table I. If these are treated as purely direct dipolar couplings, the apparent bond lengths indicated in 1 would be 1.72 Å across the C=P double bond and 1.97 Å to the directly bonded aryl

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Table II. Comparison of Tensor Elements[a]

type	observed				scaled[b]			
	σ_{11}	σ_{22}	σ_{33}	$\Delta\sigma$	σ_{11}	σ_{22}	σ_{33}	$\Delta\sigma$
$^{13}C=C^c$	108	-5	-102	210	108	-5	-102	210
$^{31}P=C^d$	473	-97	-377	850	124	-25	-98	222
$P=^{13}C^d$	188	-40	-147	334	188	-40	-147	334
$^{31}P\equiv P^e$	742	-245	-497	1239	194	-64	-130	324
$^{13}C\equiv C^f$	71	71	-143	214	71	71	-143	214
$C\equiv^{31}P^g$	198	109	-305	503	52	28	-80	132

[a] All tensor components (ppm) relative to the isotropic shifts. Low field taken as positive. [b] ^{31}P shifts scaled with eq 2 and referenced to the isotropic shift. [c] *trans*-2-Butene. [d] Compound 1. [e] 1,2-Bis(2,4,6-tri-*tert*-butylphenyl)diphosphene. [f] Methylacetylene. [g] Compound 2.

carbon. The apparent C≡P triple-bond length would be 1.58 Å. These r_{NMR} distances are on average 5% longer than distances measured by X-ray crystallography,[9] which are 1.665, 1.847, and 1.516 Å, respectively. If molecular motion can be neglected, these differences can be attributed to the anisotropy of the indirect dipolar coupling.[20,23] Using the above bond lengths, D can be calculated for the C=P, C≡P, and aryl C—P bonds and subtracted from the observed D_T values to yield ΔJ. While the absolute sign of D is known, that of D_T is not leaving an ambiguity in the value of ΔJ. Two values are possible for each of the three cases studied here, and these are reported in Table I.

Discussion

Trends in Shift Tensor Components. The CSA patterns for ^{31}P in 1 and 2 are compared to those for ^{13}C in acetylene and *trans*-2-butene[27] in Figure 2. This figure demonstrates how strikingly alike the patterns for these two nuclei are when in similar bonding arrangements. In the triple bonds the shift tensors are axially symmetric or very close to having axial symmetry, while in the doubly bonded compounds the patterns have an asymmetry parameter closer to 1. The perpendicular component of the CSA in the triple bonds falls near the intermediate component in the doubly bonded species. For both nuclei, the unique shielding element parallel to the triple bond comes to significantly higher field than the highest field element for the double bonds. Overall, the changes in the shielding tensor elements upon going from a triple bond to a double bond for ^{13}C are reproduced for ^{31}P in analogous systems.

The shift tensors for the carbons adjacent to the ^{31}P nuclei in compounds 1 and 2 are also quite interesting to compare to their organic counterparts.[27] For all but σ_{22} of the aryl carbon in 1, the ^{13}C shift tensor elements for carbons adjacent to phosphorus in these molecules tend to shift downfield in comparison to the organic systems. In compound 1, all three components for the phosphaalkene carbon have pronounced shifts to lower field in comparison to alkenes. The σ_{11} shift for the aryl carbon bonded to the phosphorus in this molecule is typical for an alkyl-substituted aromatic, while σ_{11} is shifted about 40 ppm to higher field and σ_{33} shifts 60 ppm to lower field. The -60 ppm shift for σ_{33} in 2 is characteristic of an acetylenic carbon. In C_∞ molecules, this component falls at -90 ppm for ^{13}C as the paramagnetic shielding goes to zero from symmetry considerations.[28] The shift downfield from this position is most likely due to the breaking of this symmetry by the aryl group. It is also interesting to note that the position of the σ_{11} component in the phosphalkyne carbon at 290 ppm is more similar to that found in acetylides than in acetylenes.[27] The spread of the shielding anisotropy, $\Delta\sigma = \sigma_{11} - \sigma_{33}$, is also affected by the presence of phosphorus. In 1 the phosphaalkene carbon has a $\Delta\sigma \sim 1.6$ times that in ethylene, while the adjacent aryl carbon has a $\Delta\sigma$ that is about 0.75 times as large as that in a typical aromatic ring. The $\Delta\sigma$ for the phosphaalkyne carbon is about 1.5 times as large as that in a typical alkyne.

To compare the tensorial shifts for ^{31}P and ^{13}C in these systems, the orientations of the shift tensors with respect to the molecular frame must be known. Although the data reported here do not determine the orientation of the ^{31}P shift tensors in the molecular frame, there is ample precedence from previous studies to make these assignments.[11,20] On the basis of symmetry and previous ^{13}C studies of linear and pseudolinear molecules,[28] the high-field ^{31}P tensor component in 2 must be along the triple-bond axis as stated earlier. In the phosphaalkene, the principal axis system is not so easily determined. Previous work[11] demonstrated that the high-field component in a P=P double bond is perpendicular to the π-bond nodal plane as found for ^{13}C in alkenes.[20,29] Thus, it is quite likely that σ_{33} here is perpendicular to the C=P—C plane. While the intermediate component σ_{22} probably lies closest to the C=P bond axis, it is not possible to ascertain just how much the twist from this orientation may be.

Circumstantial support for these assignments of the orientations of the ^{31}P shift tensors in the molecular frame is provided by the data for the ^{13}C shift tensors of the carbons adjacent to the phosphorus in these molecules. These orientations are determined by the dipolar couplings to ^{31}P and are in accord with previous assignments for sp²- and sp-hybridized carbons.[11,27] In the C=P double bond, σ_{22} is found to lie along the bond axis and presumably σ_{33} is perpendicular to the π-bond nodal plane. By symmetry, σ_{33} in the C≡P triple bond lies along the bond axis as confirmed by the ^{13}C chemical shift anisotropy broadened dipolar doublet line shape analysis. For the aryl carbon, σ_{11} is found to be along the C–P bond and σ_{33} is again assigned to be perpendicular to the aromatic ring in analogy to the results found for other aromatic rings. Thus, it can be seen that the orientations of the ^{13}C and ^{31}P shift tensors in these molecules are very similar when the same types of bonding for carbon and phosphorus are involved, and this in turn permits us to compare the individual tensorial shifts for these nuclei.

Comparison of ^{13}C and ^{31}P Shifts. While the anisotropic shifts for ^{13}C and ^{31}P in double- and triple-bonded situations follow parallel trends and the shift tensors are oriented similarly in the molecular frame, the anisotropies in the ^{31}P shifts are a factor of 2–4 times larger than their ^{13}C counterparts. To answer whether or not this is a consequence of a difference in the electronic structure of the multiple bonds involving phosphorus requires a more quantitative comparison of the shifts. As discussed earlier, one factor to consider is the intrinsic Z dependence on the magnitude of the chemical shift. In Table II, sets of ^{13}C tensorial shifts are compared with the appropriate ^{31}P shifts that have been scaled to the ^{13}C shift scale. This scaling is accomplished by inserting each of the ^{31}P shifts into eq 2 to arrive at an equivalent ^{13}C shift. The scaled ^{31}P shifts and the ^{13}C shifts included for comparison have been referenced to the isotropic shift of each tensor to make comparisons easier. By scaling the tensor shifts in this fashion to a common shift scale, the intrinsic differences in the shift ranges are suppressed so that the shifts may be used to ascertain the degree of similarity or dissimilarity in the bonding. Pairs of molecules to be compared in this fashion should differ by replacement of one element for another at only a single center. Thus, the ^{13}C shifts in a C=C bond are compared to the ^{31}P shifts in a P=C bond and the ^{13}C shifts in a C=P bond are compared to the ^{31}P shifts for the P=P bond. One objection to this procedure is that it compares polar to nonpolar functional groups. However, the fact that the chemical shifts for many pairs of different nuclei

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do satisfy linear relationships implies that the bond polarity effects on chemical shifts must be small or result in a constant additive or multiplicative factor.

The results of this exercise are quite revealing. For the doubly bonded species, the scaled ^{31}P and observed ^{13}C shift tensors are seen to be very similar. Given the approximate nature of this scaling process, it is quite surprising that the largest deviation is only 20 ppm between a ^{13}C tensor component and a scaled ^{31}P shift element. The agreement shows that apart from the different $\langle 1/r^3 \rangle_{np,nd}$ factors for ^{13}C and ^{31}P, the rest of the matrix elements determining the shielding are largely the same. Thus, there must be a great deal of similarity in the molecular orbitals of the C=C, C=P, and P=P double bonds. The scaling method also can be seen to have some predictive value. In our earlier paper[11] on the NMR of the P=P double bond, this approach was used to predict that the ^{13}C shift anisotropy in **1** would be 50% larger than that in an alkene. This has in fact been verified by the current work.

The σ_{11} component of the CSA in the P=P double bond was previously noted to come at significantly lower field than that for ^{13}C in analogous alkenes, even when scaled.[11] This component is approximately perpendicular to the phosphorus lone pair and the p_z orbital involved in the π bond. At that time it was hypothesized that the shift in this component could be due to a low-lying n → π^* transition involving these two orbitals. Given that this same shift in σ_{11} occurs for ^{13}C in the phosphaalkene carbon, it now seems that this shift cannot be rationalized so easily. Hopefully, ab initio calculations in the future will be able to shed some light on the electronic origin of this paramagnetic shift.

The comparison of the scaled ^{31}P shifts for the phosphaalkyne to the ^{13}C CSA for the acetylenic carbons of methylacetylene in Table II is not as good. Only the σ_{11} values turn out to be close in this case. At present, this is not believed to be evidence for dissimilarity in the electronic structures of these triple bonds nor a failure of the method used for scaling these shifts. Rather, the disagreement is likely to be due to the fact that these two molecules are not similar enough in structure. Ideally, a compound such as phenylacetylene or diphenylacetylene should be used for comparison. Attempts to acquire the ^{13}C tensors from powder spectra for the alkyne carbons in these molecules were unsuccessful because of the overlap of the phenyl and acetylenic carbon resonances. MAS sideband patterns were also uninformative, as both molecules give as many as eight resonances for each carbon and the lines overlap badly. One is left with methylacetylene as the best available molecule for comparison.

This is unfortunate in that shift anisotropies for acetylenic carbons are quite sensitive to how the local symmetry is broken by the ligands. This is especially true for the σ_{33} shift, as the paramagnetic component in this shift is solely due to the breaking of the C_∞ symmetry by the ligand. Whereas in acetylene this component falls at -90 ppm,[28] the addition of a methyl group in methylacetylene shifts it to -74 ppm. A phenyl group would be expected to produce an even larger paramagnetic shift, as the symmetry breaking will be more pronounced. Thus, it is not surprising that the σ_{11} components as compared do not agree well. The aryl group in **2** also breaks the degeneracy of the σ_{11} and σ_{22} components, while in methylacetylene these components are the same by symmetry. Because of these considerations, the comparison of the scaled ^{31}P CSA for **2** to that for ^{13}C in methylacetylene may only be as good as can be expected. The discrepancies in the compared shifts are in the expected directions, and the overall pattern of the shifts and trends from double to triple bonds are similar. Thus, even though the quantitative comparison is not as good for the triple bonds as in the double bonds, a high degree of similarity between the bonding in phosphaalkynes and acetylenes is indicated. Measurement or ab initio calculation of shift tensors for better model compounds is needed to ascertain whether the differences seen in the scaled shifts imply any difference between the electronic structure of the C=C and C=P triple bonds.

Other Observations. Table I contains the apparent anisotropies in the indirect dipolar or J couplings between ^{13}C and ^{31}P in compounds **1** and **2**. Little is understood about these anisotropies

at present. The numbers reported are similar to those found for ^{31}P-^{31}P ΔJ's in diphosphines and diphosphenes.[11,23] For all of these systems it can be noted that the anisotropy in J must be either over a factor of 2 larger than the direct dipolar coupling or about 1 order of magnitude less. Given that this situation has now been seen for at least six indirect coupling tensors involving ^{31}P, it seems likely that the latter situation holds. If this is the case, the MAS spectra determine the sign of the isotropic J couplings to be positive, consistent with solution NMR results.[30] Data of this type may be helpful in developing a better theoretical understanding of J anisotropies, which is important as these are a source of error in bond length determinations by NMR methods that are difficult to assess experimentally.

In this same vein it should be pointed out that it has been traditionally *assumed* that vibrational averaging of direct dipolar couplings is only important when light nuclei such as protons are involved and that for pairs of heavy nuclei these corrections can be neglected. While this seems plausible, calculations by Henry and Szabo[31] indicate in organic systems that low frequency vibrational modes in molecular crystals can make very significant contributions to such averaging. This type of motion involving entire molecules or unit cells will affect all dipolar couplings without regard to the mass of the individual nuclei involved. Therefore, the apparent anisotropies in the indirect couplings reported here should only be taken as upper limits to the actual ΔJ values. It is an open question as to whether or not one can assume motional averaging to be insignificant even for pairs of ^{13}C and ^{31}P nuclei, and this point merits further scrutiny.

The unusual apparent noise riding on top of the powder spectra shown in Figure 2 also deserves some discussion. As noted earlier, this seems to be a real feature of the signals and not an experimental artifact. If the samples consisted of large crystallites, such an effect could be a result of not having a uniform distribution of orientations. However, as the samples are quite finely powdered, this cannot be the case. The only plausible mechanism that has been identified is a field-induced ordering of the microcrystallites themselves when placed in the magnetic field. Spiess et al. have noted a dramatic effect of this type in the proton spectra of some layered intercalation compounds.[32] Just how such a field-induced ordering takes place is unclear in these samples. It is important to note that if such ordering is strong, the distortions in the powder line shapes may also affect the sideband intensities in MAS spectra. This could result in significant errors in tensors derived from the sideband intensities.[33]

Conclusions

The shielding patterns, trends in shift tensor elements, and orientations of the shielding tensors in the molecular frame for ^{31}P in double and triple bonds to carbon are very similar to those for ^{13}C in analogous organic systems. Quantitative comparison of the ^{31}P shift tensor elements to related ^{13}C shift tensors has been accomplished by a scaling procedure that removes the intrinsic Z dependence of the chemical shifts. When the scaled shift tensors for phosphorus in double bonds are compared to ^{13}C shift anisotropies for alkenes, the individual elements agree very well. The comparison for ^{31}P in a phosphaalkyne reported here is not as good, but it is believed that this may be due to the fact that appropriate model ^{13}C tensors are not available at this time and not due to any significant differences in the electronic structures of the C=C and C=P triple bonds. In the phosphaalkene **1**, the σ_{11} ^{13}C component is found to have a large downfield shift relative to σ_{11} in alkenes. The same shift in the scaled ^{31}P σ_{11} tensor element is found when a diphosphene is compared to **1**. Overall, these observations indicate that P=C and P=P bonds are very much like C=C bonds and that P=C bonds are similar to C=C bonds.

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The patterns in shifts in the shielding tensor elements upon heteroatom substitution or on going from doubly to triply bonded arrangements have been rationalized with very qualitative ideas about chemical shifts. While high-level ab initio calculations now accurately reproduce experimentally observed chemical shifts, such calculations have not as yet produced a great deal of insight into the factors determining chemical shifts. An in-depth exposition of the electronic factors responsible for these shifts and an explanation at an ab initio level for the success of the shift scaling procedure used here then remain as challenging problems for electronic structure theorists. It is expected that development of an understanding at the ab initio level of the trends in tensorial shifts noted in work of the type presented here will be useful in developing better insight from these electronic structure calculations.

Resonance Raman Pursuit of the Change from Fe^{II}-O_2 to Fe^{III}-OH via Fe^{IV}=O in the Autoxidation of Ferrous Iron-Porphyrin

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Abstract: Resonance Raman (RR) and visible absorption spectra were observed for autoxidation intermediates of ferrous tetramesitylporphyrin [(TMP)Fe^{II}] to the ferric hydroxy derivative [(TMP)Fe^{III}OH] via (TMP)$Fe^{II}O_2$, (TMP)Fe^{III}OOFe^{III}(TMP), and (TMP)Fe^{IV}=O. The O–O stretching [$\nu(O_2)$] and Fe^{II}-O_2 stretching [$\nu(Fe^{II}$-$O_2)$] Raman bands were simultaneously observed at 1171 and 522 cm^{-1}, respectively, for the (TMP)$Fe^{II}O_2$ in toluene solution at –100 °C for the first time. The present data together with the reported IR data for the solution samples indicate a linear inverse correlation between $\nu(O_2)$ and $\nu(Fe^{II}$-$O_2)$ frequencies similar to that between $\nu(CO)$ and $\nu(Fe^{II}$-CO), but the data from heme proteins fall off the line. Upon raising the sample temperature to –70 °C, formation of (TMP)Fe^{III}OOFe^{III}(TMP) was confirmed by ^{1}H NMR and its visible absorption spectrum was determined. However the peroxo-bridged dimer was so photolabile that it was decomposed into (TMP)Fe^{IV}=O by laser illumination even at –70 °C, and therefore, no oxygen isotope sensitive RR band assignable to (TMP)Fe^{III}OOFe^{III}(TMP) was identified. (TMP)Fe^{IV}=O was also photolabile and yielded the photoproduct, the same as the case of thermal decomposition, but (TMP)Fe^{IV}=O gave the Fe^{IV}=O stretching [$\nu(Fe^{IV}$=O)] Raman band at 843 cm^{-1}, which is in agreement with the value reported for the five-coordinate oxoferryl complex. The reduction rate of (TMP)Fe^{IV}=O to (TMP)Fe^{III}OH was different between the toluene-h_8 and -d_8 solutions, suggesting that it proceeds via hydrogen abstraction from toluene. Presumably, the Fe^{IV}=O bond has a partial radical character, which increases upon electronic excitation, and this is the reason why decomposition of (TMP)Fe^{IV}=O is accelerated by laser illumination.

A mechanism of dioxygen activation by iron(II) porphyrin has attracted chemists' attention in relation to elucidation of the catalytic mechanism of various heme enzymes.[2a,b] The presence of the oxy ferrous form (PFe$^{II}O_2$; P denotes a porphyrin dianion) was revealed spectroscopically for cytochrome P-450[3a–c] and cytochrome oxidase[4a–c] as well as for hemoglobin (Hb) and myoglobin (Mb), although structures of the successive reaction intermediates such as the oxoferryl form (PFe^{IV}=O) have not been well documented yet. Physicochemical properties of PFe^{IV}=O in peroxidases have been extensively investigated with Mössbauer,[5a–c] NMR,[6] ENDOR,[7] EXAFS,[8] and resonance Raman (RR) techniques[9a–f] and are compared with those of model

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