Characterization of a Novel Triply Bonded Iminophosphenium Cation by Nitrogen-15 and Phosphorus-31 Solid-State NMR Spectroscopy

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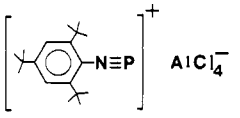
Abstract: The first stable compound containing a nitrogen-phosphorus triple bond, $[2,4,6\text{-tri-}t\text{-Bu-}C_6H_2N{\equiv}P]^+[AlCl_4]^-$ (**1**), has been investigated by ^{15}N and ^{31}P solid-state NMR spectroscopy. Analysis of dipolar chemical shift NMR spectra for static powdered samples of **1** has provided the three principal components of the ^{15}N and ^{31}P chemical shift tensors and allowed the determination of their orientations in the molecular frame of reference. Both chemical shift tensors are slightly nonaxially symmetric with ^{15}N and ^{31}P chemical shift anisotropies of 421 ± 4 ppm and 581 ± 4 ppm, respectively. The most shielded principal component of both chemical shift tensors is oriented along the N,P bond axis. Comparison of the observed ^{15}N and ^{31}P chemical shift tensors for **1** with experimental and theoretical results for related compounds suggests that the electronic environment surrounding the N,P moiety of **1** is similar to other systems containing a formal triple bond.

Introduction

Recently Niecke et al.[1] reported the synthesis of the first stable compound with a nitrogen-phosphorus triple bond. The iminophosphenium cation (**1**) was characterized by ^{31}P, ^{13}C, and ^{1}H



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NMR in toluene/benzene-d_6 and benzene-d_6 solutions as well as by X-ray crystallography.[1] The X-ray diffraction results indicate that this system crystallizes from toluene with one molecule of toluene as solvate. The orthorhombic unit cell (P_{bca}) contains eight crystallographically equivalent molecules. The CNP bond angle is approximately 177° with a N,P bond length of 1.475 Å.[1] This combination of near linear geometry and short N,P internuclear separation was observed to be consistent with the bond length calculated for $P{\equiv}NH^+$ (r_{NP} = 1.476 Å);[2] thus, Niecke et al.[1] argue that the N,P bond of **1** has a high degree of triple-bond character.

Although ^{13}C chemical shift tensors have been reported for numerous systems in which carbon nuclei are involved in multiple bonding,[3-15] analogous results for nitrogen chemical shift tensors[3,4,9,12-14,16-21] and phosphorus chemical shift tensors[3,17,22,23] have been lacking. In addition, it has become apparent that while theoretical calculations of ^{13}C chemical shift parameters have become reasonably accurate,[3,11,24-26] it is often difficult to obtain accurate theoretical values for the principal components of ^{15}N and ^{31}P chemical shift tensors, particularly when these nuclei are involved in multiple bonds.[3,24-29]

To characterize the nitrogen and phosphorus chemical shift tensors in a system containing a N,P triple bond, we have prepared the iminophosphenium cation (**1**) with and without ^{15}N isotopic enrichment for study by solid-state ^{15}N and ^{31}P dipolar chemical shift NMR spectroscopy. This represents the first example of a phosphorus(III) compound containing a multiple N,P bond studied by solid-state NMR spectroscopy. Our results will be compared to experimental and theoretical results for several compounds containing nitrogen and/or phosphorus involved in a triple bond.

Theory

Complete characterization of the chemical shift parameters for a nucleus in a molecule requires a knowledge of both the magnitudes and orientations of the three principal components of the chemical shift tensor (δ_{ii}, i = 1-3) in the molecular frame of reference. Therefore, in general, six parameters are required: the three principal components and three Euler angles. The traditional approach for obtaining such information has been to study single crystals via solid-state NMR spectroscopy and determine the magnitudes and orientation of the three principal components of

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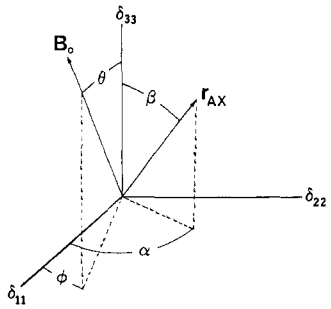

Figure 1. Angles α and β define the orientation of the dipolar vector, r_{AX}, in the principal axis system of the chemical shift tensor. The orientation of the magnetic field vector, B_0, with respect to the principal axis system of the chemical shift tensor is defined by the angles θ and ϕ.

the chemical shift tensor in the crystal axis system from chemical shift versus crystal rotation plots.[8,30-33] A much simpler method is applicable when the nuclei of interest are part of an isolated spin pair, AX, and are coupled to one another by the direct dipolar interaction. Using this technique, known as dipolar chemical shift solid-state NMR spectroscopy,[34-37] one can obtain the magnitude of the three principal components of the chemical shift tensor and two of the three angles that define the orientation of the chemical shift tensor (Figure 1). Specifically, the angles α and β can be determined by comparing observed powder NMR line shapes with those calculated by using eq 1.[34-37] Here $\nu_A(m_X)$ is the resonance

$$\nu_A(m_X) = (\gamma_A B_0/2\pi)[1 - [\sigma_{11}\sin^2\theta\cos^2\phi + \sigma_{22}\sin^2\theta\sin^2\phi + \sigma_{33}\cos^2\theta]] - m_X(R - \Delta J/3)[1 - 3(\sin\beta\sin\theta\cos(\phi-\alpha) + \cos\beta\cos\theta)^2] - m_X J_{iso} \quad (1)$$

frequency for the A nucleus, m_X is the spin state of the X nucleus, R is the direct dipolar coupling constant, and ΔJ is the anisotropy in the indirect spin–spin coupling.

$$R = (\mu_0/4\pi)(h/4\pi^2)\gamma_A\gamma_X\langle r_{AX}^{-3}\rangle \quad (2)$$

$$\Delta J = (J_{\parallel} - J_{\perp}) \quad (3)$$

The polar angles θ and ϕ define the orientation of the principal axis system of the chemical shift tensor with respect to the applied magnetic field, B_0. Equation 1 implies that the J tensor is axially symmetric and that $J_{\parallel}$ is aligned with the dipolar vector, r_{AX}. The principal components of the chemical shielding tensor are defined such that $\sigma_{33} \geq \sigma_{22} \geq \sigma_{11}$. Experimentally one measures a difference in the shielding constants between nuclei in the compound of interest and some reference compounds, i.e., chemical shifts. The principal components of the chemical shift tensor are defined such that $\delta_{11} \geq \delta_{22} \geq \delta_{33}$. All remaining symbols in eqs 1–3 have their usual meaning.

The spin of the X nucleus determines the number of subspectra observed in a dipolar chemical shift NMR spectrum of the A nucleus. If the X nucleus is a spin $^1/_2$ nucleus, there are two such subspectra whose detailed line shapes are related to the mutual orientations of the dipolar and chemical shift tensors as specified in eq 1. If, however, the X nucleus is a spin 1 nucleus, eq 1 may not be strictly valid if the quadrupolar coupling constant of the X nucleus, $\chi(X)$, is large compared to its corresponding Larmor frequency, $\nu_L(X)$.[38,39] On the basis of established results for isocyanides (R—N≡C),[16,40,41] we anticipate that the magnitude of χ for the ^{14}N nucleus in **1** should be relatively small; thus, distortions in the ^{31}P NMR spectrum should be minimal. Under these conditions, the static solid-state NMR spectrum for the ^{31}P nuclei will consist of three subspectra with the observed dipolar splittings being related to the values of σ_{ii}, α, β, R, J_{iso}, and ΔJ specified in eq 1. The approach used here is to estimate these parameters from an experimental NMR spectrum of the A nuclei and then to refine these values by computer simulation of the NMR spectrum on the basis of eq 1. We define the chemical shift anisotropy, $\Delta\delta$, as the width of the A spin static NMR spectrum in the absence of dipolar couplings (i.e., $\delta_{11} - \delta_{33}$). The asymmetry parameter of the chemical shift tensor, η, is defined as $(\delta_{22} - \delta_{11})/(\delta_{33} - \delta_{iso})$ and is restricted to values between 0 and 1.

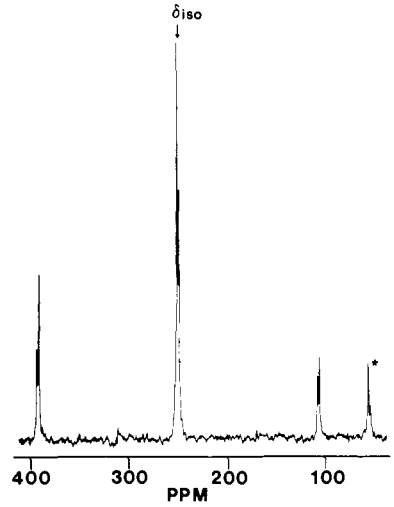

Figure 2. ^{15}N CP/MAS NMR spectrum for a ^{15}N-enriched sample of **1**. The isotropic chemical shift of a small amount of impurity is labeled with an asterisk (*).

Experimental Section

The samples of **1** were prepared in a glovebox under an inert atmosphere according to the published results of Niecke et al.[1] The 1,3,5-tri-*tert*-butylbenzene and 2,4,6-tri-*tert*-butylaniline were procured commercially (Aldrich Chemical Co.). ^{15}N-enriched (95%) HNO_3 was purchased from the Sigma Chemical Co. and was reacted with 1,3,5-tri-*tert*-butylbenzene to form 2,4,6-tri-*tert*-butyl[^{15}N]nitrobenzene.[42] This sample was then reduced as outlined in ref 42 to give the corresponding ^{15}N-enriched amine for preparation of **1**. It was determined by ^{31}P CP/MAS NMR (vide infra) that samples of **1** prepared according to the procedure in ref 1 were a mixture of solvated and nonsolvated material. Pure samples of the toluene solvate of **1** were prepared by recrystallization of the crude product from toluene. Prolonged evacuation of the samples was shown to cause partial solvate dissociation.

^{15}N and ^{31}P solid-state NMR spectra were recorded at 20.30 and 81.03 MHz, respectively, on a Bruker MSL-200 spectrometer (B_0 = 4.7 T). Samples were ground into a fine powder (~300 mg) and packed into zirconium oxide rotors (7 mm o.d.) in the glovebox. Rotors were topped with solid caps that had been coated with a medium-tipped felt marker around the inner edge to form an air tight seal. Samples packed in this manner were found to be stable on the laboratory bench for periods in excess of 1 month. All NMR spectra were acquired with high-power proton decoupling and ^1H, ^{15}N, and ^{31}P $\pi/2$ pulse widths of 2.5–5.5 μs. For the ^{15}N NMR experiments, the conditions of the Hartmann–Hahn match were optimized by using a sample of doubly ^{15}N enriched am-

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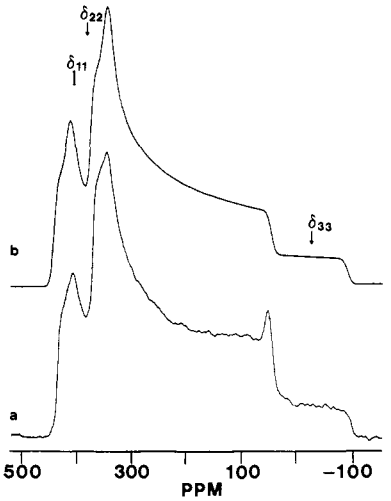

Figure 3. Experimental (a) and simulated (b) ^{15}N NMR spectra for a static powder sample of ^{15}N-enriched **1**.

monium nitrate. Nitrogen-15 chemical shifts were referenced with respect to $NH_3(l)$ at 0 ppm by setting the observed chemical shift of the $^{15}NH_4^+$ ion of NH_4NO_3 at 23.8 ppm (293 K). A sample of $NH_4H_2PO_4$ was used for optimizing the conditions for the ^{31}P CP NMR experiments. Phosphorus-31 chemical shifts were referenced with respect to H_3PO_4 (85%) at 0 ppm by setting the ^{31}P chemical shift of $NH_4H_2PO_4$ at 0.81 ppm (293 K). Contact times of 8–10 ms were used for all ^{15}N and ^{31}P CP experiments. CP/MAS NMR spectra were acquired with MAS rates of 1–4 kHz with acquisition times of approximately 50–400 ms. The static CP ^{31}P NMR spectra were acquired with the addition of a π pulse applied with the broadband channel after the cross-polarization period to generate a Hahn echo.[43] This was necessary to alleviate spectral distortions associated with acoustic ringing of the NMR probe. Typical delays between the end of the contact pulse and the π pulse were 30 μs. The filter width was opened to its maximum value of 2 MHz to reduce the dead time associated with filter ringing. Acquisition times for the static NMR spectra were approximately 30 ms. Sensitivity enhancements corresponding to line broadening of 5 and 70 Hz were applied to the MAS and static FIDs, respectively, prior to Fourier transformation.

Calculation of theoretical powder NMR spectra based on eq 1 were performed on a VAX 8800 computer using the interpolation scheme of Alderman et al.[44] The resulting theoretical NMR spectra were then convoluted with a Gaussian line-broadening function.

Results and Discussion

Nitrogen-15 NMR Spectra. A ^{15}N CP/MAS NMR spectrum of the ^{15}N-enriched (95%) sample of **1** is shown in Figure 2. The isotropic resonance for **1**, $\delta_{iso} = 248.1 \pm 0.5$ ppm, is a well-resolved doublet with a spin–spin coupling $^1J(^{15}N,^{31}P)_{iso} = 36 \pm 2$ Hz. The observation of a simple doublet is consistent with the X-ray diffraction results which indicate that this system crystallizes with eight crystallographically equivalent molecules per unit cell.[1] This is advantageous since crystallographic nonequivalence can cause difficulties in the analysis of NMR spectra of static powdered samples.[21] The ^{15}N CP/MAS NMR spectrum also indicated that a small amount of impurity was present in this sample (i.e., small asymmetric doublet at 52.4 ppm). On the basis of the intensities of the respective ^{15}N NMR signals, the relative amount of this impurity is small, and therefore it should not lead to significant distortions in the static ^{15}N NMR spectrum of this sample.

The static ^{15}N NMR spectrum for the isotopically enriched sample of **1** is shown in Figure 3a. Inspection of this NMR spectrum indicates six well-defined discontinuities characteristic of a nonaxially symmetric chemical shift tensor powder pattern split by dipolar coupling with a spin $^1/_2$ nucleus. On the basis of the N,P bond length determined from X-ray diffraction experiments,[1] 1.475 Å, the direct dipolar coupling constant, R, for the $^{15}N,^{31}P$ spin pair was calculated to be −1538 Hz (see eq 2). If the dipolar coupling constant is constrained to −1538 Hz and one assumes a negligible anisotropy in J, then simulations based on eq 1 indicate that $\alpha = 45.0 \pm 2.0°$ and $\beta = 16.4 \pm 2.0°$. This value of β places the most shielded principal component of the ^{15}N chemical shift tensor 16.4° off the N,P bonding axis. However, on the basis of local symmetry and results reported for related molecules,[3,4,9,12,16–20] one might anticipate a β value equal to 0°. Our data can accommodate this possibility if we assume that the effective dipolar coupling constant, R', is different from the value calculated on the basis of X-ray diffraction data. Two mechanisms by which the apparent dipolar splitting would be reduced are (1) contributions from anisotropy in J and (2) averaging due to molecular motions (i.e., librations and vibrations). To account for these effects, one can write an effective dipolar coupling constant, R', in terms of an order parameter, S, an anisotropic spin–spin coupling, ΔJ, and a static value for the dipolar coupling constant, R. Simulations of the static ^{15}N NMR spectrum shown in Figure 3a with $\beta = 0°$ indicate that R' is $\pm 1353 \pm 35$ Hz. In determining this value of the effective dipolar coupling constant, it was found that computer simulations of the observed splittings in the ^{15}N static NMR spectrum could be improved slightly by assuming that $^1J(^{15}N,^{31}P)_{iso}$ is positive. However, given the inherent line width of the ^{15}N static NMR spectrum and the small magnitude of $^1J(^{15}N,^{31}P)_{iso}$, 36 ± 2 Hz, any definitive conclusion about the sign is tenuous.

If one assumes $\beta = 0°$ and no motional averaging, i.e., $S = 1$, then the magnitude of ΔJ can be calculated from eq 4. Since

$$R' = S(R - \Delta J/3) \quad (4)$$

the value of R based on X-ray crystallographic results is −1538 Hz and R' can be positive or negative, ΔJ can be calculated to be −555 or −8763 Hz. These two J anisotropies are very different, and since the NMR experiment is only sensitive to the absolute value of the effective dipolar coupling tensor (eq 4), a definitive assignment cannot be made. However, considering the fact that $|^1J(^{15}N,^{31}P)_{iso}|$ is only 36 Hz and that the indirect coupling involves a first row element, it is difficult to envisage a J tensor where $J_\parallel$ and $J_\perp$ are different by over 8000 Hz. Other authors have encountered the same dilemma;[22,45,46] we make a tentative conclusion that the effective dipolar coupling constant for the $^{15}N,^{31}P$ spin pair is negative, and this assumption imposes a *limit* on the magnitude of ΔJ of −555 Hz.

An alternative explanation for the observed reduction of the dipolar coupling constant, R, for the $^{15}N,^{31}P$ spin pair of **1** is the presence of vibrational and librational motions (i.e., $S \neq 1$).[47–49] Henry and Szabo[47] have demonstrated that vibrations which affect the AX internuclear separation and librations which influence the orientation of the dipolar vector can significantly decrease the magnitude of the dipolar coupling constant, R. They concluded that librational averaging of the dipolar interaction is more important than vibrational averaging, particularly as the size and torsional flexibility of the molecule increase. If we assume $\beta = 0°$ and ΔJ is negligible, then the 12% reduction in R from that calculated on the basis of the X-ray bond length must be attributed to motional averaging. Unfortunately, detailed X-ray diffraction data for the toluene solvate of **1** have not been published, so that librational information is currently unavailable. However, X-ray diffraction results for the structurally related *p*-benzenediazonium sulfonate indicate that the largest amplitude librations occur about the N–N–Cl–C4–S direction with a mean angle of 8 ± 1°.[50] If

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Table I. Nitrogen-15 and Phosphorus-31 Chemical Shift Parameters for the Iminophosphenium Cation (**1**)[a]

nucleus	δ_{11}	δ_{22}	δ_{33}	δ_{iso}	Δ_δ	R'	J_{iso}[b]	β	η
$^{15}N{\equiv}^{31}P$	400	366	-21	248.3 (248.1)	421	-1353	+35	0	0.13
$^{31}P{\equiv}^{15}N$	308	196	-273	77.0 (78.5)	581	-1353	+35	0	0.32
$^{31}P{\equiv}^{14}N$	308	196	-273	77.0 (78.5)	581	960	-24	0	0.32

[a] Nitrogen and phosphorus chemical shifts are referenced in ppm with respect to NH_3(l) (293 K) and 85% H_3PO_4 (293 K), respectively. The observed chemical shifts from CP/MAS experiments are shown in parentheses. Errors in the three principal components of the ^{15}N and ^{31}P chemical shift tensors are ±3 and ±1.5 ppm, respectively. [b] Tentative assignment of the sign based on simulations using eq 1.

Table II. Absolute Nitrogen Chemical Shielding Parameters for Several Compounds Containing Nitrogen Involved in a Triple Bond[a]

compd	σ_{11}	σ_{22}	σ_{33}	σ_{iso}	$\Delta\sigma$
1	-156	-122	265	-3.3	421
HCN obs[52]	-215	-215	348	-27	563
CH_3CN obs[4]	-142	-142	346	21	488
CH_3NC[b]	10	10	370	130	360
N≡N obs[18]					603
obs[53]	-319	-319	335	-101	654
P≡N obs[3,17]	-698	-698	350	-349	1047
calc[28]	-849	-849	341	-452	1190
C_6H_5CN calc[27]	-216	-181	247	-50	463
p-R-C_6H_5CN obs[c]	-149	-130	243	-12	392

[a] Absolute shielding constant of NH_3(l) at 293 K, 244.6 ppm.[51] [b] Experimental results from liquid crystal NMR studies.[16] Reported error in $\Delta\sigma$ is ±70 ppm. [c] Solid-state NMR results for R = t-Bu derivative.[12]

we assume that the symmetry axis of **1** traces the surface of a cone, then the half-angle of the cone, Ψ, may be estimated from

$$\cos^2 \Psi = (2S + 1)/3 \quad (5)$$

Application of eq 5 with the values of R and R' previously discussed indicates a value for Ψ of 16.4°. It should be noted that this represents the maximum value of the angle Ψ for a single mode of libration in the absence of anisotropy in J. The effective dipolar coupling constant for the $^{15}N,^{31}P$ spin pair is given together with the ^{15}N chemical shift parameters and isotropic J in Table I. The calculated ^{15}N static NMR spectrum using these values is shown in Figure 3b. We estimate that the errors in the three principal components of the ^{15}N chemical shift tensor are ±3 ppm. Note, however, that the δ_{ii} values are reported as determined from the NMR spectrum in Figure 3a and are not corrected for librational averaging.

The three principal components of the ^{15}N chemical shift tensor of compound **1** were converted to an absolute chemical shielding scale and are given in Table II. The nitrogen shielding parameters for several other compounds containing nitrogen involved in a triple bond are included in Table II for comparison. With the exception of methyl isocyanide, all of these compounds contain a nitrogen that is bonded to one atom only. To our knowledge, nitrogen chemical shift parameters for compounds similar to **1** are presently unavailable.

Theoretical discussions of chemical shielding are usually based on Ramsey's theory, which was reformulated by Saika and Slichter[54] and Pople.[55] In these models, the principal components of the shielding constant are considered to be a sum of a diamagnetic term, σ_{ii}^d, and a second-order paramagnetic term, σ_{ii}^p. The diamagnetic term is always positive, leading to shielding of the nucleus, while the paramagnetic term is invariably negative,

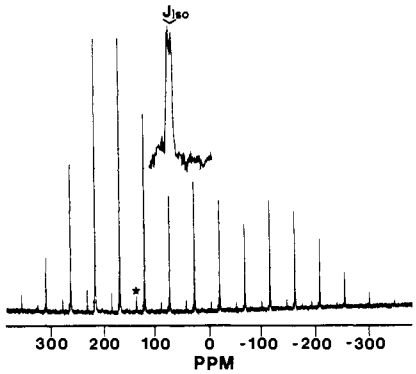

Figure 4. ^{31}P CP/MAS NMR spectrum for a ^{15}N-enriched sample of **1**. A small amount of impurity in this sample gives rise to an independent series of spinning side bands; the isotropic chemical shift is labeled with an asterisk (*). The insert shows an expansion near the isotropic ^{31}P resonance signal of **1**, demonstrating the splitting due to J coupling between ^{31}P and ^{15}N.

leading to a deshielding of the nucleus. It is well-known that for nuclei such as nitrogen and phosphorus variations in the paramagnetic term are largely responsible for the orientation dependence of chemical shielding.[3,12,20,23,28,29] For example, in a linear molecule the paramagnetic contribution to the chemical shielding constant is zero when the C_∞ axis of the molecule is oriented parallel to B_0 and a maximum when the molecule is perpendicular to B_0. In contrast, the diamagnetic term shows relatively small variations with molecular orientation in B_0. The implication is that for linear or pseudolinear molecules, the most shielded component of the chemical shielding tensor, σ_{33}, corresponds to the orientation in which the "symmetry" axis is along B_0. Variations in this component of the shielding constant will be solely due to variations in σ^d if the molecule is linear. If the molecule is not perfectly linear, the paramagnetic term may contribute to σ_{33}. From the data in Table II, it is clear that σ_{33}(N) is relatively constant in simple diatomics, acetonitrile and methyl isocyanide. In fact, σ_{33} for these molecules is close to the nitrogen free atom value determined by Malli and Froese, 325.5 ppm.[56] When the molecular symmetry decreases as in **1**, the most shielded component of the ^{15}N chemical shielding tensor, σ_{33} = 265 ppm, is significantly smaller than the corresponding values for the simpler molecules in Table II. The implication of this result is that the paramagnetic contribution to σ_{33} of **1** is probably greater than -50 ppm.

Although the presence of a methyl group in acetonitrile and methyl isocyanide does not significantly influence the magnitude of σ_{33} compared to the corresponding values in HCN, N_2, and NP, the perpendicular components of the shielding tensor for CH_3CN and CH_3NC change substantially. For example, $\sigma_\perp$ (σ_{11} and σ_{22}) of the ^{15}N chemical shielding tensor of acetonitrile is more shielded than the corresponding value for HCN by over 75 ppm. Further reduction of the molecular symmetry, as for **1**, leads to the observation of nonequivalent values for the σ_{11} and σ_{22} principal components of the ^{15}N chemical shielding tensor, -156 and -122 ppm, respectively. In addition, these values are substantially larger (i.e., smaller σ^p) than the perpendicular principal components of the nitrogen shielding tensors of N≡N and N≡P, -319 and -698 ppm, respectively. Since the magnitude of these principal components of the nitrogen shielding tensor are related to $\sigma \rightarrow \pi^*$ transition energies,[28] this observation suggests that $\Delta E_{\sigma\rightarrow\pi^*}$ increases from N≡P to N≡N to **1**.

Finally, it is interesting to point out the similarity of the three principal components of the nitrogen shielding tensor of **1** to corresponding results for *p-tert*-butylbenzonitrile.[12] For example, the most shielded principal components (σ_{33}) differ by only 22 ppm in these systems, whereas the differences for σ_{11} and σ_{22} are

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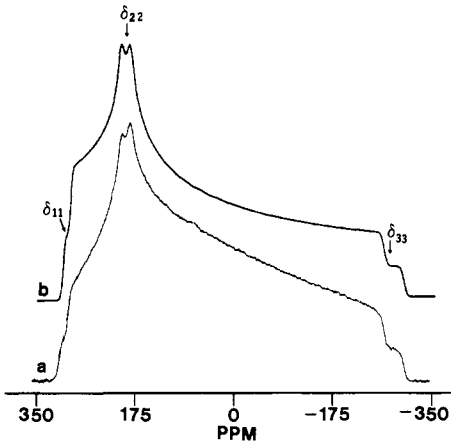

Figure 5. Experimental (a) and simulated (b) ^{31}P NMR spectra for a static powder sample of ^{15}N-enriched **1**.

only 7 and 8 ppm, respectively. Note, however, that the comparison of the σ_{11} and σ_{22} nitrogen tensor elements of **1** to those of the benzonitrile derivative may be fortuitous since the orientations of the perpendicular components in these systems are not known.

Phosphorus-31 NMR Spectra. The phosphorus-31 CP/MAS spectrum for the ^{15}N isotopically enriched sample of **1** is shown in Figure 4. The isotropic spin–spin coupling constant could be determined directly from Figure 4 and was found to be $^1J(^{15}N,^{31}P)_{iso} = 35 \pm 2$ Hz, in close analogy to the value determined from ^{15}N CP/MAS experiments (Figure 2). The large breadth of spinning side bands suggests that the ^{31}P chemical shift anisotropy is quite large. Indeed, the width of the static ^{31}P NMR spectrum shown in Figure 5a exceeds 600 ppm. When the static ^{31}P NMR spectrum was acquired, it was found that a Hahn echo[43] was essential to alleviate severe distortions in the line shape. We attribute this to the fact that the ^{31}P nucleus has three strong contacts (316 pm)[1] with the chlorine nuclei of the tetrachloroaluminate counterions. Chlorine has two magnetically active isotopes with spin $^3/_2$ and the direct dipolar coupling constants, R_{PCl}, can be calculated (see eq 2) to be 151 and 126 Hz for coupling with ^{35}Cl and ^{37}Cl, respectively. This leads to a very rapid decay of the time domain ^{31}P FID (i.e., the signal completely decayed in less than 400 μs) and hence to substantial line broadening in the Fourier transformed NMR spectrum.

In analogy to our interpretation of the ^{15}N static NMR spectrum, we anticipated a value for the effective ^{15}N,^{31}P dipolar coupling constant of −1353 Hz [assuming $^1J(^{15}N,^{31}P)_{iso}$ is +36 Hz]. Indeed, the observed dipolar splittings in Figure 5a are consistent with this value. The three principal components of the ^{31}P chemical shift tensor obtained from these simulations are given in Table I; the simulated static ^{31}P NMR spectrum is shown in Figure 5b. The value for β is 0°, in analogy to the ^{15}N NMR results. This places the most shielded element of the ^{31}P chemical shift tensor along the N,P bonding axis and is consistent with intuitive arguments based on symmetry. Line broadening of 800 Hz was applied to the simulated ^{31}P static NMR spectrum to accurately portray the experimental ^{31}P static NMR spectrum. For the corresponding simulated ^{15}N static NMR spectrum (Figure 3b), line broadening of only 200 Hz was sufficient for accurate spectral simulation. In view of the previous discussion, this observation can be attributed to intermolecular dipolar interactions involving the chlorine nuclei of the tetrachloroaluminate counterions and the phosphorus and nitrogen nuclei in neighboring molecules.

A sample of unenriched **1** (i.e., containing an "isolated" ^{14}N,^{31}P spin pair) was the initial sample to be prepared by our group for study by solid-state NMR. When we obtained a ^{31}P CP/MAS NMR spectrum of this sample, we were surprised to observe two independent sets of spinning side bands with isotropic chemical shifts of 78.5 and 64.8 ppm. Upon recrystallization of this sample from toluene, we observed only a single isotropic resonance at 78.5 ppm. This is similar to the ^{31}P chemical shift reported by Niecke et al. for **1** dissolved in a solution of toluene/benzene-d_6, δ_{iso} = 79.3 ppm.[1] Interestingly, prolonged evacuation of the sample vesicle containing the recrystallized compound **1** resulted in an increase in the intensity of the lower frequency ^{31}P NMR resonance. Thus, we conclude that the higher frequency ^{31}P NMR resonance (δ_{iso} = 78.5 ppm) is associated with the toluene-solvated iminophosphenium cation studied by X-ray crystallography,[1] whereas the lower frequency ^{31}P NMR resonance (δ_{iso} = 64.8 ppm) arises from the nonsolvated **1**. Further attempts to isolate the nonsolvated material in pure form have been unsuccessful, although the solvated species can be prepared readily with reasonably high purity (Figures 2 and 4).

Acquisition of a static ^{31}P NMR spectrum for a recrystallized ^{14}N,^{31}P sample of the toluene solvate of **1** was performed in similar fashion to that for the ^{15}N,^{31}P sample. By use of a value of β = 0° and the δ_{ii} values in Table I, the effective dipolar coupling constant for the ^{14}N,^{31}P spin pair was determined to be 960 Hz. In determining this value, we assumed a value for of −24 Hz for $^1J(^{14}N,^{31}P)_{iso}$, which was calculated from the corresponding value observed for the ^{15}N-enriched sample of **1**. The ratio observed for the effective dipolar coupling constants, $R'(^{15}N,^{31}P)$ versus $R'(^{14}N,^{31}P)$ is 1.409, which compares very well to the value determined from the ratio of $\gamma(^{15}N)/\gamma(^{14}N)$, 1.403. Therefore, we conclude that the ^{31}P chemical shift tensor parameters in Table I are reliable and that the high-field approximation[38,39] is valid for the ^{14}N nuclei involved in the N,P bond of **1**. Finally, on the basis of the arguments presented for the ^{15}N NMR results, we anticipate that librational motions are more important in reducing the dipolar coupling constant, R, than is ΔJ. However, if we assume no motional averaging (i.e., S = 1) and a value for R = 1097 Hz (r_{PN} = 1.475 Å), ΔJ for the ^{14}N,^{31}P spin pair can be calculated to be 411 or 6171 Hz if the value of R' is taken to be positive or negative, respectively. On the basis of earlier discussions, we conclude that an *upper limit* on the J anisotropy for the ^{14}N,^{31}P spin pair is approximately 411 Hz.

There are very few cases in the literature in which ^{31}P chemical shift tensors for compounds containing P(III) centers involved in multiple bonds have been reported.[3,17,22] To our knowledge, the only experimental values for the ^{31}P chemical shift parameters of the phosphorus center of a N,P triple bond are those reported for the diatomic molecule, N≡P, from gas-phase microwave data.[17] The absolute ^{31}P shielding parameters for this compound (experimental[17] and theoretical[28]) as well as the experimental ^{31}P NMR results for **1** and theoretical[28] results for P≡P are given in Table III. The most shielded principal component of the ^{31}P chemical shielding tensor, σ_{33}, for the linear molecules N≡P and P≡P is approximately 970 ppm. This is very close to the value for the free P atom, 961.1 ppm,[56] and is consistent with our previous discussion. As the symmetry of the molecular environment decreases, such as for compound **1**, shielding of the σ_{33} principal component decreases to 601 ppm. The implication of this result is that $\sigma^p \neq 0$ for the σ_{33} principal component of the ^{31}P chemical shielding tensor of **1** and, in fact, the paramagnetic contribution to σ_{33} is probably greater than −350 ppm. The σ_{11} and σ_{22} principal components of the ^{31}P chemical shielding tensor of **1** are considerably different (over 100 ppm), and this is reflected in the value of the asymmetry parameter, $\eta = 0.32 \pm 0.02$. The ^{31}P chemical shielding anisotropy for **1**, 581 ± 4 ppm, is significantly smaller than values of 1376 and 1903 ppm previously reported for the diatomic molecules N≡P and P≡P, respectively. The results in Table III indicate that this difference is primarily

Table III. Absolute Phosphorus Chemical Shielding Parameters for **1** and Two Diatomic Molecules N≡P and P≡P

compd	σ_{11}	σ_{22}	σ_{33}	σ_{iso}	$\Delta\sigma$
1[a]	21	132	601	251	580
P≡N obs[3,17]	−406	−406	970	53	1376
calc[28]	−497	−497	966	−10	1463
P≡P calc[28]	−934	−934	969	−299	1903

[a] Absolute shielding constant of H_3PO_4 (85%), 328.35 ppm, determined relative to σ_{abs} of PH_3, 594.45 ppm.[57]

associated with changes in the perpendicular components (i.e., σ_{11} and σ_{22}). As previously discussed, the perpendicular components are dominated by paramagnetic contributions from low-lying $\sigma \rightarrow \pi^*$ transition energies.[28] Thus, in analogy to the ^{15}N NMR results, the ^{31}P shielding parameters suggest that the $\Delta E_{\sigma\rightarrow\pi^*}$ transition energy for compound **1** is larger than the corresponding values for N≡P and P≡P. It is interesting to point out that the magnitude of the ^{31}P chemical shielding anisotropy reported here, 581 ± 4 ppm, is intermediate to values reported for P(III) centers involved in single and double bonds.[22] Accordingly, the observed isotropic ^{31}P chemical shift, δ_{iso} = 78.5 ppm, follows the same empirical trend (i.e., δ_{iso}(P—X)$\langle\delta_{iso}$(P≡X)$\langle\delta_{iso}$(P=X)) that Niecke et al. used to interpret solution ^{31}P NMR data of **1** and its precursor.[1]

Conclusions

Dipolar chemical shift solid-state NMR spectroscopy has been used to characterize the ^{15}N and ^{31}P chemical shift tensors for a novel system (**1**) containing a N,P triple bond. The presence of librational motion has been postulated to account for the decrease in the observed value of the dipolar coupling constant, R, with perhaps a small but indeterminate contribution from ΔJ. Our results indicate that the most shielded principal component of both the ^{15}N and ^{31}P chemical shift tensors, δ_{33}, is oriented parallel to the N,P bond axis. The ^{15}N and ^{31}P chemical shift anisotropies for **1** are 421 ± 4 and 581 ± 4 ppm, respectively. Comparison of the results obtained here with chemical shift tensors reported for the nitrogen and phosphorus centers in related compounds suggests that the electronic environment around the N,P moiety of **1** is similar to that of other systems containing a triple bond. Interestingly, the asymmetry of the molecular environment in **1** has a substantial effect on the three principal components of both the ^{15}N and ^{31}P chemical shift tensors. The most striking example of this is the implication that the most shielded component of the ^{31}P chemical shift tensor for **1** has a paramagnetic contribution in excess of −350 ppm. It is hoped that the information provided here will stimulate the interest of theoreticians to investigate nitrogen and phosphorus shielding parameters in more complex organophosphorus and organonitrogen compounds.

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