# **Inorganic Chemistry**

## Syntheses of Diphenylaminodiazidophosphane and Diphenylaminofluoroazidophosphane

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**Supporting Information** 

**ABSTRACT:** Diphenylaminodiazidophosphane  $(C_6H_5)_2NP-(N_3)_2$  was synthesized from the corresponding dihalides  $(C_6H_5)_2NPX_2$  (X = F, Cl) and  $(CH_3)_3SiN_3$ , and was characterized by vibrational and multinuclear NMR spectroscopy. The intermediate compound  $(C_6H_5)_2NPF(N_3)$  was also observed by NMR spectroscopy in solution. Some physical properties and reactions of all these compounds are discussed.



The amount of research into azide-containing compounds has increased rapidly over the past decade, due largely to advances in the field of highly energetic high nitrogen materials, and many novel main group azides have been synthesized, including several of phosphorus. Phosphorus triazide had been reported, and its vibrational spectra and <sup>31</sup>P NMR spectrum had been given,<sup>1</sup> but later work brought most of these data into question when the rapid thermal decomposition of  $P(N_3)_3$  in solution near room temperature and new <sup>31</sup>P NMR data were published.<sup>2,3</sup> Otherwise, apart from photoelectron spectra,<sup>4</sup> only some computational results have been reported for phosphorus triazide.<sup>5,6</sup> Later it was reported that  $P(N_3)_3$  was reacted with  $N_3^-$  in an attempt to generate  $P(N_3)_4^-$ ;<sup>7</sup> however, there was no experimental evidence offered that either  $P(N_3)_3$  or  $P(N_3)_4^-$  was present.

Several phosphorus(III) monoazides are also known:  $(CF_3)_2P(N_3)$ , which decomposes between 0 °C and ambient temperature and sometimes unexpectedly even at -196 °C;<sup>8</sup>  $(C_6H_5)_2P(N_3)$ , which decomposes explosively at ~14 °C;<sup>9</sup>  $F_2P(N_3)$  is unstable and occasionally explodes at 25 °C;<sup>10</sup> and  $Cl_2P(N_3)$  and  $Br_2P(N_3)$ , both of which decompose slowly at 35 °C.<sup>2,3</sup> With respect to ionic monoazido-P(III) species, it is worth noting that no evidence was found for the  $PF_3(N_3)^-$  anion in an NMR study.<sup>11</sup> On the other hand, there has been a crystal structure reported for the monoazido-P(III) cationic species,  $[(CH_3)_3Si]_2N=P-N_3^+$ , as its  $GaCl_4^-$  salt which is only stable up to -40 °C.<sup>12</sup>

More relevant to this work, much less is known about P(III)diazido compounds. There is a brief report on two very unstable compounds,  $(C_6H_5)P(N_3)_2$ , which starts to decompose before its preparative reaction is complete, and  $(Me_3C_6H_2)P(N_3)_2$ , which is only stable for a few hours in solution,<sup>13</sup> and the room temperature stable [ $(t-Bu)_3C_6H_2$ ]P- $(N_3)_2$ , which was characterized by X-ray crystallography.<sup>13</sup> In addition, a phosphorus(III) diazido tetra-substituted-imidazo-



lium species [(2-diazidophosphino)-4,5-dimethyl-1,3-bis(1-methylethyl)-1*H*-imidazolium cation] has been identified via its X-ray crystal structure and fully characterized spectroscopically as its triflate salt,<sup>14</sup> although it slowly decomposes even at -31 °C. Another more recent publication describes the Raman, IR, multinuclear NMR spectra, and crystal structure of the [(2-diazidophosphino)-4,5-dichloro-1,3-bis(2,6-methylethyl-phenyl)-1*H*-imidazolium cation] as its triflate salt<sup>15</sup> which is stable at -40 °C, but tends to decompose slowly upon warming to room temperature.

In contrast to the amount of research conducted on P(III)azido compounds, there has been considerable research on phosphorus(V)-azido compounds. Although phosphorus pentaazide was previously reported in 1975,<sup>1</sup> this claim was subsequently retracted.<sup>16</sup> A <sup>31</sup>P NMR study on several mixed phosphorus(V)-chloro-azido species [P(V)Cl<sub>(5-n)</sub>(N<sub>3</sub>)<sub>n</sub>, n = 4, 3, 2] in pyridine solution, however, has been reported.<sup>17</sup> The existence of the P(N<sub>3</sub>)<sub>6</sub><sup>-</sup> anion was initially described in 1967 as its P(C<sub>6</sub>H<sub>5</sub>)<sub>4</sub><sup>+</sup> salt<sup>18</sup> and has been extended from alkali metal cations such as Na<sup>+16</sup> to the polynitrogen N<sub>5</sub><sup>+</sup> cation,<sup>19</sup> and the [(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>P=N=P(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>]<sup>+</sup> cation,<sup>20</sup> for example. Various mixed phosphorus(V)-chloro-fluoro-azido anions [PCl<sub>x</sub>F<sub>y</sub>(N<sub>3</sub>)<sub>z</sub><sup>-</sup>, x + y + z = 6] in CH<sub>2</sub>Cl<sub>2</sub> solutions have also been described.<sup>11,21,22</sup> The formation of many P(V)-azido cations has been reported including P(N<sub>3</sub>)<sub>4</sub><sup>+</sup> and the mixed P(N<sub>3</sub>)<sub>n</sub>(CH<sub>3</sub>)<sub>4-n</sub><sup>+</sup> (n = 3, 2, 1) SbCl<sub>6</sub><sup>-</sup> compounds,<sup>23</sup> as well as P(N<sub>3</sub>)<sub>n</sub>(C<sub>6</sub>H<sub>5</sub>)<sub>4+n</sub><sup>+</sup> (n = 3, 2, 1) SbCl<sub>6</sub><sup>-</sup> salts<sup>24</sup> for which various properties have been described.

Additional compounds have been made where three azido groups are attached to a P(V) atom, i.e., the long known  $OP(N_3)_3$  and  $SP(N_3)_3$  compounds which have recently had their crystal structures determined.<sup>25</sup> Whereas the mixed  $OPF(N_3)_2$ ,  $OPF_2(N_3)$ , and  $SPF_2(N_3)$  compounds have been

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known since 1972,<sup>10</sup> OPF(N<sub>3</sub>)<sub>2</sub> has only recently been investigated via photolytic and thermal decomposition.<sup>26</sup> Other phosphorus(V)-azido compounds such as  $S=P[N=PRPh_2]_2(N_3)$  and  $S=P[N=PRPh_2](N_3)_2$  have been reported,<sup>27</sup> as have several cyclic P–N phosphorus-azido  $RR'(P-N)_m(N_3)_n$  species.<sup>28–30</sup>

Whereas several structural studies on certain  $M(III)(N_3)_3/M(III)(N_3)_4^-$  and  $M(V)(N_3)_5/M(V)(N_3)_6^-$  systems, [M = As, Sb, Bi] have been reported [refs 31, 7, and 32 (and references therein)], none have been found for either  $P(N_3)_3$  or any  $P(N_3)_4^-$  compounds.

Many covalent azido compounds have a reputation for being unpredictably unstable with respect to sudden decompositions (as described above), but even these can be handled safely using appropriate precautions and techniques. This is true primarily because the N<sub>3</sub> group is highly endothermic with a positive heat of formation,<sup>33</sup> which explains why azido compounds have found use in propellants and explosive formulations. The purpose of this work, however, was the preparation and characterization of diphenylaminodiazidophosphane, thereby contributing to the understanding of the relatively poorly known class of diazidophosphanes.

## 2. RESULTS AND DISCUSSION

Both of the two dihalide compounds,  $(C_6H_5)_2NPCl_2$  and  $(C_6H_5)_2NPF_2$ <sup>34</sup> are thermally stable to at least 100 °C, and it was expected that the corresponding diazide compound could also be isolated.  $(C_6H_5)_2NPCl_2$  was first considered as a precursor for the preparation of  $(C_6H_5)_2NP(N_3)_2$ . Although the  $(C_6H_5)_2NPCl_2$  compound had been previously reported,<sup>34</sup> its synthesis has been improved in this study.

**2.1.** Syntheses of  $(C_6H_5)_2NPCl_2$ ,  $(C_6H_5)_2NPF_2$ , and  $(C_6H_5)_2NP(N_3)_2$ . The synthesis of  $(C_6H_5)_2NPCl_2$  was conducted in benzene according to reaction 1 under strictly anhydrous conditions after it was discovered that moisture hydrolyzes not only the PCl<sub>3</sub> starting material, but also the desired  $(C_6H_5)_2NPCl_2$ , which probably affected the initial purity and yields in the past studies.<sup>34</sup>

$$PCl_3 + (C_6H_5)_2NH + xs N(C_2H_5)_3$$

$$\xrightarrow{C_6H_6} (C_6H_5)_2NPCl_2 + NH(C_2H_5)_3Cl$$
(1)

After vacuum distillation of the crude product at 135 °C and collection of the final product at 25 °C, the isolated yield was increased to over 74% compared to the previously reported 55%. In this work the vibrational and NMR spectra of the clear, colorless, viscous liquid  $(C_6H_5)_2NPCl_2$  were recorded and showed no evidence of any impurities, *vide infra*. When it was discovered that this material was not suitable for the direct synthesis and isolation of pure  $(C_6H_5)_2NPCl_2$ , reagent was replaced by  $(C_6H_5)_2NPF_2$ .

The  $(C_6H_5)_2NPF_2$  was prepared under anhydrous conditions in acetonitrile according to reaction 2 as reported in the literature:<sup>34</sup>

$$(C_6H_5)_2NPCl_2 + 2NaF \xrightarrow{CH_3CN} (C_6H_5)_2NPF_2 + 2NaCl$$
(2)

The  $(C_6H_5)_2NPF_2$  product is a somewhat less viscous material than the  $(C_6H_5)_2NPCl_2$  starting material and has a higher vapor pressure at room temperature, requiring its collection at a temperature of -22 °C well below its melting point of 11 °C to avoid large losses of the material upon vacuum distillation in a short-path-length apparatus. The yield of this clear, colorless liquid was again improved, in this case to 86% as compared to the literature report of 78%.<sup>34</sup> The compound's identity was verified via vibrational and NMR spectroscopy which showed no impurites, *vide infra*.

Initially, the synthesis of  $(C_6H_5)_2NP(N_3)_2$  was attempted by reacting  $(C_6H_5)_2NPCl_2$  with NaN<sub>3</sub> in acetonitrile, as shown in reaction 3, a method which has been known to result in Cl/N<sub>3</sub> exchange in many other systems.

$$(C_6H_5)_2NPCl_2 + 2NaN_3$$

$$\xrightarrow{CH_3CN} (C_6H_5)_2NP(N_3)_2 + 2NaCl$$
(3)

However, this approach resulted in only a very small amount of  $(C_6H_5)_2NP(N_3)_2$  as determined by NMR spectroscopy. Even in the presence of CsF as a catalyst, which has often been used in other similar systems, reaction 4 progressed only slowly to give  $(C_6H_5)_2NP(N_3)_2$  over extended periods of time.

$$(C_6H_5)_2 \text{NPCl}_2 + 2\text{NaN}_3$$

$$\xrightarrow{CH_3CN} (C_6H_5)_2 \text{NP}(N_3)_2 + 2\text{NaCl}$$
(4)

The thermal instability at ambient temperature and low volatility at lower temperatures of  $(C_6H_5)_2NP(N_3)_2$ , however, did not allow its isolation and separation from the NaCl byproduct, either by filtration in acetonitrile, or by distillation either at ambient temperature under a nitrogen atmosphere or at lower temperatures *in vacuo*. The greatest drawback in the generation of  $(C_6H_5)_2NP(N_3)_2$  by this method was the exceedingly long time that was required for the reaction to go to completion.

A superior method for the preparation of  $(C_6H_5)_2NP(N_3)_2$ involved the generation of a volatile byproduct which could be more easily removed *in vacuo* along with the solvent from the desired less volatile product. Therefore,  $(C_6H_5)_2NPF_2$  was reacted instead with  $(CH_3)_3SiN_3$  in  $CH_3CN$ . Initial efforts using the neat reagents resulted in a very slow reaction, but when a small amount of CsF was added as a catalyst, the reaction in  $CH_3CN$  solution proceeded much more rapidly as shown in reaction 5.

$$(C_{6}H_{5})_{2}NPF_{2} + 2(CH_{3})_{3}SiN_{3}$$

$$\xrightarrow{CH_{3}CN}_{CsF} (C_{6}H_{5})_{2}NP(N_{3})_{2} + 2(CH_{3})_{3}SiF$$
(5)

A low temperature NMR study as a function of time revealed that reaction 5 was complete in a matter of only a few hours. When the volatile  $(CH_3)_3SiF$  and  $CH_3CN$  solvent were pumped off at temperatures between -20 and -30 °C, the poorly soluble CsF catalyst settled to the bottom of the reactor, and the clear colorless  $(C_6H_5)_2NP(N_3)_2$  was easily cannulated from the small amount of CsF to give a pure product.

**2.2. Raman Spectroscopic Results.** Raman spectroscopy at -60 °C was used to characterize  $(C_6H_5)_2NP(N_3)_2$  (Figure 1). The Raman spectra at 20 °C of  $(C_6H_5)_2NPF_2$  and  $(C_6H_5)_2NPCl_2$  were also recorded for comparison (Figures 2 and 3).

Although vibrational data have been published for  $P(N_3)_3$ and  $P(N_3)_{5,}^{1}$  the former are questionable, and those for the latter must be discounted in view of the subsequent <sup>31</sup>P NMR data and chemical analyses.<sup>2,3</sup> According to previous low level HF/6-31+G\* calculations for phosphorus triazide,  $P(N_3)_{3,}^{6}$  the in-phase and out-of-phase antisymmetric  $N_3$  stretching



**Figure 1.** Raman spectrum of  $(C_6H_5)_2NP(N_3)_2$  recorded in a thinwalled Teflon FEP tube at -60 °C. Bands for the Teflon FEP tube are designated with \*.



Figure 2. Raman spectrum of  $(C_6H_5)_2NPF_2$  recorded in a Pyrex tube at 20 °C.



Figure 3. Raman spectrum of  $(C_6H_5)_2\text{NPCl}_2$  recorded in a Pyrex tube at 20  $^\circ\text{C}.$ 

vibrations and the symmetric  $N_3$  stretching vibrations were predicted to occur at 2520 and 2558 cm<sup>-1</sup> and at 1338 and 1378 cm<sup>-1</sup>, respectively.

Some selected Raman data calculated using configuration 1 (see below in section 2.3) are listed together with the experimental data in Table 1 for  $(C_6H_5)_2NP(N_3)_2$ , along with experimental data for  $(C_6H_5)_2NPF_2$  and  $(C_6H_5)_2NPCl_2$ . A

complete list of the experimental and calculated vibrational frequencies for these three compounds can be found in the accompanying Supporting Information Table S1.

Experimentally, the presence of the azido groups in  $(C_6H_5)_2NP(N_3)_2$  can be easily seen in the Raman spectrum from the  $\nu_{as}$  in-phase and  $\nu_{as}$  out-of-phase stretching modes which occur, respectively, at 2136 and 2119  $\text{cm}^{-1}$  (Figure 1), and which are absent in the analogous difluoro- and dichlorocompounds. This conclusion is clearly supported by the calculated values for the diazido-compound (Table 1). Similar bands for the N3 group have been observed for the in-phase and out-of-phase antisymmetric N3 stretching vibrations of  $As(N_3)_3$  at 2128 and 2103 cm<sup>-1</sup>, respectively, and of  $Sb(N_3)_3$  at 2123 and 2079 cm<sup>-1</sup>, respectively.<sup>35</sup> In the case of  $(C_6H_5)_2NP_ (N_3)_2$  a relatively broad band was observed at 1257 cm<sup>-1</sup> characteristic for the symmetric N<sub>3</sub> stretching vibration. Although there are bands in the Raman spectra for  $(C_6H_5)_2NPF_2$  and  $(C_6H_5)_2NPCl_2$  in this same region, the band at 1257 cm<sup>-1</sup> has a comparatively larger intensity than those in the other spectra. The frequency of  $1257 \text{ cm}^{-1}$ compares well with similar bands found at 1257, 1244/37  $cm^{-1}$  and 1263, 1248  $cm^{-1}$  for  $As(N_3)_3$  and  $Sb(N_3)_3$ , respectively.35

Several other bands were observed in the  $(C_6H_5)_2NP(N_3)_2$ spectrum that could be assigned with confidence to modes not predominantly associated with the  $(C_6H_5)_2N$  group. (1) Of the three expected N<sub>3</sub> bending frequencies, only two modes, the  $\delta$ N<sub>3</sub> in-phase/out-of-plane and  $\delta$  N<sub>3</sub> in-phase/in-plane vibrations (coupled with a P–N stretching band) at 550 and 509  $cm^{-1}$ , respectively, were observed in agreement with those previously reported for As(N<sub>3</sub>)<sub>3</sub>.<sup>35</sup> A third mode, the  $\delta$  N<sub>3</sub> out-of-phase/ in-plane vibration, at  $\sim 639$  cm<sup>-1</sup> was calculated to be too low an intensity to be observed. (2) Four P-N stretching vibrations involving only the  $P-[N(N_2)]_2$  group were expected. One calculated band at 678 cm<sup>-1</sup> was not observed because of an overlap at  $\sim$ 702 cm<sup>-1</sup> with a much stronger differently assigned band (see below). A second closely calculated band at 639 cm<sup>-1</sup> was simply not observed because of extremely weak intensity. On the other hand, two other calculated bands at 530 and 492 cm<sup>-1</sup> were observed at 533 and 509 cm<sup>-1</sup>, respectively, (albeit the latter is coupled with an N3 bending vibration as stated above). (3) A number of other predicted frequencies containing a contribution from the P-N stretching mode of the PN( $C_6H_5$ )<sub>2</sub> group coupled with other vibrations [such as  $\delta$ N<sub>3</sub>,  $\delta_{\text{sciss}}$  N<sub>3</sub>, or  $\delta_{\text{sciss}}$  NC<sub>2</sub>] of the molecule could be matched with experimental bands. Some calculated couplings of this P-N mode with other modes in the molecule, however, were not observed due to low calculated intensities, and are listed in Table S1 of the Supporting Information. (4) One particular vibration (the  $\nu_s$  (C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>N-P-[N(N<sub>2</sub>)]<sub>2</sub> skeletal mode involving the P atom with the amido-N and the two azido-N atoms) could be unambiguously assigned to the band at 702 cm<sup>-1</sup>. Also, the  $\delta_{sciss}$  PX<sub>2</sub> (X = F, N<sub>3</sub>, Cl) modes were found at 400, 282, and 191 cm<sup>-1</sup>, respectively. The rest of the N<sub>3</sub> deformations and N-P-N skeletal deformation modes were calculated to be very weak and are presumably hidden underneath other  $(C_6H_5)_2N$  group bands.

The symmetric and antisymmetric stretching vibrations for the PF<sub>2</sub> group in the Raman spectrum of  $(C_6H_5)_2NPF_2$  were observed at 809 and 761 cm<sup>-1</sup>. These frequencies are lower (as expected) than those found for the P–F stretching frequencies in liquid PF<sub>3</sub> at 890 and 840 cm<sup>-136,37</sup> and at 893.2 and 858.4 cm<sup>-1</sup> in gaseous PF<sub>3</sub>.<sup>38</sup> Raman frequencies for the PF<sub>2</sub> group

## Table 1. Selected Experimental and Calculated Raman Data for $(C_6H_5)_2NPX_2$ Compounds, $[X = Cl, F, and N_3]$

(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> NPCI <sub>2</sub>	(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> NPF <sub>2</sub>	(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> NP(N <sub>3</sub> ) <sub>2</sub>		Approximate		
Experimental <sup>[a]</sup>	Experimental [a]	Experimental <sup>[a]</sup> Calculated <sup>[b]</sup>		Mode		
			B3LYP/6-311+ G(d,p)	Description		
		2136 (10.8)	2161 (156)	$v_{as}$ in-phase $N_3$		
		2119 (8.0)	2148 (93)	vas out-of-phase N3		
		1257 (9.7,ol)	1290 (24)	v <sub>s</sub> in-phase N <sub>3</sub>		
		n.o.	1269 (2)	v <sub>s</sub> out-of-phase N <sub>3</sub>		
1195 (34.8)	1204 (40.4)	1202 (26.7)	1209 (58)	Vas N-C2		
· · ·	. ,	· · ·	1162 (30)	$(v_s N-C_2 \text{ and } \delta (C_6H_5))$		
1173 (12.9)	1176 (11.3) 1160 (12.0)	1177 (12.5) 1159 (12.8)	1153 (49)	coupled with		
1159 (9.3)			1146 (96)	$v P-N(C_6H_5)_2$		
917 (1.1)	920 (0.3)	920 (1.4)	· ·	$(v P-N(C_eH_5)_2)$ coupled with		
			934 (2)	δ- N-Co		
n.o.	n.o.	n.o.	866 (3)	vas IV C <sub>2</sub>		
				$\delta$ (C <sub>c</sub> H <sub>c</sub> ) deformations		
	809 (3 3 br)					
	761 (3.3, br)					
	701 (3.3,61)	20	679 (1)			
		702 (17 0)	670 (1)	$V_{\rm s} P$ -[N(N <sub>2</sub> )] <sub>2</sub>		
		702 (17.9)	673 (16)	$V_{s} (C_{6}H_{5})_{2}N-P-[N(N_{2})]_{2}$		
		n.o.	639 (0.6)	$\left\{ v_{as} P-[N(N_2)]_2 \text{ with} \right\}$		
			. ,	$\delta$ N <sub>3</sub> out-of-phase/in-plane		
n.o.	n.o.	n.o.	596 (2)	$\delta_{s wag} P-N(C_6H_5)_2$		
		550 (5.1)	547 (0.05)	$\left\{\begin{array}{c} \delta \ N_3 \text{ in-phase/out-of-plane} \right.$		
			546 (0.05)			
		533 (8.9) 530 (5)		$\int v_{as} P-[N(N_2)]_2$		
		. ,	•••	with N <sub>3</sub> twisting		
533 (2.7)	534 (6.2)	527 (8.0)	515 (3)	$v P-N(C_6H_5)_2$ with		
				$\delta_{sciss} N-C_2$ and $\delta (C_6H_5)$		
n.o.	n.o.	n.o.	505 (4)	$\delta_{\text{umb}} P-\underline{N}-C_2$		
		509 (5.3) 492 (27)	$v_{s} P-[N(N_{2})]_{2}$ with			
			· · /	$\delta$ N <sub>3</sub> in-phase/in-plane		
495 (14.2)				$v_s PCI_2$		
472 (7.8)				$v_{as} PCI_2$		
~440 (4.8,sh)	445 (2.3)	448 (1.1)	431 (0.8)	$\delta_{\text{wag}} \text{ P-N}(C_6 \text{H}_5)_2$		
393 (4.8)	400 (6.9,ol)	400 (2.1sh)	395 (3)	$\delta_{umb} N-\underline{P}-X_2$		
	400 (6.9)			$\delta_{sciss}  \text{PF}_2$		
311 (2.9)	318 (6.1)	316 (5.1)	306 (2)	$\delta_{twist} P-N(C_6H_5)_2$		
		282 (4.0)	291 (10)	$\delta_{sciss} P(N_3)_2$		
191 (7.2,sh)				$\delta_{sciss} PCI_2$		

<sup>*a*</sup>Experimental Raman frequencies in cm<sup>-1</sup> with intensities (in parentheses) in arbitrary units normalized to the most intense band in each spectrum set at 100.0; ol = overlap, br = broad, sh = shoulder, n.o. = not observed. <sup>*b*</sup>Calculated Raman frequencies are given in cm<sup>-1</sup> with intensities (in parentheses) in Å<sup>4</sup> amu<sup>-1</sup>. A scaling factor of 0.96 was used. <sup>*c*</sup>Raman bands for the Teflon FEP sample container were found in the  $(C_6H_5)_2NP(N_3)_2$  spectrum at 1384 cm<sup>-1</sup> (3.4), 1303 cm<sup>-1</sup> (3.7,sh), 1226 cm<sup>-1</sup> (6.2,sh), 735 cm<sup>-1</sup> (12.2), 611 cm<sup>-1</sup> (4.0), 570 cm<sup>-1</sup> (3.7), 388 cm<sup>-1</sup> (2.6), and 292 cm<sup>-1</sup> (2.0) but are not listed.

have been reported for PF<sub>2</sub>Cl at 857 and 829 cm<sup>-1</sup> and for PF<sub>2</sub>Br at 853 and 825 cm<sup>-1</sup>.<sup>39,40</sup> Raman bands for solid PF<sub>2</sub>I at -197 °C have been observed at 862 and 807 cm<sup>-1</sup>.<sup>41</sup> whereas infrared frequencies for the PF<sub>2</sub> group in Ar matrix isolated PF<sub>2</sub>I at 4.2 K were found at 843 and 835 cm<sup>-1</sup>.<sup>42</sup> The infrared spectrum of the Ar matrix isolated radical °PF<sub>2</sub> showed bands at 839.3 and 834.0 cm<sup>-1</sup>.<sup>42</sup> Infrared frequencies for the antisymmetric and symmetric PF<sub>2</sub> group in matrix isolated PF<sub>2</sub>H were found at 839.7 and 827.0 cm<sup>-1</sup>, respectively.<sup>42</sup> The

lowering of the  $PF_2$  frequencies in  $(C_6H_5)_2NPF_2$  can be ascribed to the relatively strong electron-donating effect of the  $(C_6H_5)_2N$  ligand as compared to the more electron-withdrawing halogens in  $PF_2X$ , where X = F, Cl, Br, and I. The assignment of a band found at 400 cm<sup>-1</sup> for  $(C_6H_5)_2NPF_2$  can reasonably be made to the  $PF_2$  scissoring mode. This assignment is in accord with bands at 411, 391, and 365 cm<sup>-1</sup> in  $PF_2Cl$ ,  $PF_2Br$ , and  $PF_2I$ , respectively.<sup>39-43</sup> For  $(C_6H_5)_2NPCl_2$  the symmetric and antisymmetric PCl<sub>2</sub> stretching modes are assigned to 495 and 472 cm<sup>-1</sup>, respectively. Values of 515 and 504 cm<sup>-1</sup> in the vapor phase Raman<sup>38</sup> as well as 507 and 493 cm<sup>-1</sup> in the vapor phase IR spectra<sup>44</sup> have been reported for PCl<sub>3</sub>. For liquid PFCl<sub>2</sub>, the symmetric and antisymmetric PCl<sub>2</sub> stretching vibrations are found at 522 and 498 cm<sup>-1</sup>, respectively.<sup>39</sup> Similar frequencies around 521 cm<sup>-1</sup> were observed in the infrared spectrum of gaseous PFCl<sub>2</sub>.<sup>45</sup> For the Ar matrix isolated <sup>•</sup>PCl<sub>2</sub> radical, frequencies at 525 and 452 cm<sup>-1</sup> have been reported, although the assignments have been reversed for the symmetric and antisymmetric PCl<sub>2</sub> vibrations in the literature.<sup>46</sup> The bending vibration for PCl<sub>2</sub> in  $(C_6H_5)_2NPCl_2$  was found at 191 cm<sup>-1</sup>, comparable to that found for PFCl<sub>2</sub> at 199 and 200 cm<sup>-1.39,43,45</sup>

The assignments for the symmetric and antisymmetric stretching frequencies depend on the PX<sub>2</sub> bond angle where a crossing of the symmetric and antisymmetric vibrational frequencies occurs at a bond angle of roughly 90°.<sup>47</sup> It does not seem very likely that the PF<sub>2</sub> or PCl<sub>2</sub> angle would be significantly greater than 90° in which case the antisymmetric stretching mode could begin to be lower in frequency than the symmetric one. Although two N<sub>3</sub> groups are not exactly comparable to two Cl atoms, the computational calculations conducted in this study (see below) indicate that the N<sub>azido</sub>-P-N<sub>azido</sub> bond angle is 90.5°, thus making assignments other than those given here rather unlikely.

**2.3. Computational Results.** As a part of this research,  $(C_6H_5)_2NP(N_3)_2$  was studied computationally via Gaussian 09, Revision A.02 at the B3LYP/6-311+G(d,p) level of theory,<sup>48</sup> and three main conformations were identified as minima on the potential energy surface at 298 K. The preferred configuration is shown in Figure 4. The only major differences among the three structures are in the orientations of the two azido groups with respect to each other on the pseudotetrahedral coordinated phosphorus atom. The predicted Gibbs energy difference between the highest and lowest energy conformations is only 1.6 kcal/mol, which implies that the three calculated structures have virtually the same energy at room



**Figure 4.** Calculated structure of configuration 1 for  $(C_6H_5)_2NP(N_3)_2$  at the B3LYP/6-311G(p,d) level of theory.<sup>48</sup> Selected bond distances [Å]: P24–N1 1.715, P24–N25 1.757, P24–N26 1.782. Selected bond angles [deg]: N25–P24–N26 90.49, N1–P24–N25 101.16, N1–P24–N26 105.14. Angles [deg] between planes: C2–C13–N1 and C13–N1–P24 174.58; C2–N1–P24 and N1–P24–C13 173.99; C13–N1–C2 and N1–C2–P24 173.83. Distance [Å]: N1 above plane C2–C13–P24 0.053.

temperature within the limits of the computational method. This is not unexpected for a molecule in which the azido groups are fluxional<sup>32</sup> and can rotate with low barriers about the phosphorus–nitrogen bonds.

Overall the calculated bond distances between the phosphorus atom and each of the two nitrogen<sub>azido</sub> atoms are similar for each of the configurations 1-3 with values of  $1.75 \pm$ 0.01 Å for one of the bonds and  $1.79 \pm 0.02$  Å for the second. In comparison, the bond lengths between the phosphorus and the nitrogen<sub>amido</sub> atoms were all shorter at  $1.71 \pm 0.01$  Å for all three isomers. The specific P–N<sub>azido</sub> bond lengths,  $N_{\alpha}$ –N<sub> $\beta$ </sub>–N<sub> $\gamma$ </sub> lengths and angles, as well as bond lengths and angles for the C<sub>2</sub>NP fragment of configuration 1 can be found in Table S5 in the Supporting Information. The just mentioned calculated bond length values compare favorably with crystallographic studies for a number of phosphorus-azido bond lengths in the range 1.673-1.753 Å, whether they are for phosphorus(III)azido groups present in a cation,  $^{12,14,15}$  covalent P(V)-azido molecules,<sup>25,27</sup> or cyclic P(V)N-azido compounds.<sup>28-30</sup> The calculated nitrogen<sub>azido</sub>-phosphorus-nitrogen<sub>azido</sub> bond angles for the three  $(C_6H_5)_2NP(N_3)_2$  configurations showed more variation with a value of  $90.5^{\circ}$  for configuration 1 and values of 97.8° and 95.5° for configurations 2 and 3, respectively. These values can be compared with experimental X-ray structure values between 96.4° and 113.4°.<sup>12,14,15,25,27-30</sup>

The calculated vibrational frequencies of configuration 1, however, had the best match with the experimental Raman values. Additionally, the calculations showed that the C2NP fragment was essentially planar for configuration 1 with the sum of the  $C_2NP$  angles being 359.7°. (The corresponding sums for the  $C_2NP$  angles for configurations 2 and 3 were 359.6° and 359.8°, respectively, which again show the structural similarities of the  $C_2NP$  fragment for all three configurations.) This finding is consistent with X-ray results for (CH<sub>3</sub>)<sub>2</sub>NPF<sub>2</sub> and  $(CH_3)_2NPCl_2$  where the sums of the  $C_2NP$  angles were found to be  $360.0(10)^{\circ}$  and  $359.9(4)^{\circ}$ , respectively.<sup>49,50</sup> This results in a virtually planar C<sub>2</sub>NP fragment in which the central nitrogen atom is located only 0.053 Å above the plane defined by the two carbons and the phosphorus atom. The significantly shorter nitrogen<sub>amido</sub>-phosphorus bond when compared to the longer nitrogen<sub>azido</sub>-phosphorus bonds indicates that some partial double bond character is responsible for the near planarity of the C<sub>2</sub>NP fragment.

2.4. NMR Spectroscopic Results. Further characterization of  $(C_6H_5)_2NP(N_3)_2$  was accomplished via multinuclear NMR spectroscopy. The primary nucleus used for the investigation was <sup>31</sup>P. An initial report<sup>1</sup> for the chemical shift of the related  $P(N_3)_3$  compound resulted in a value for what was later determined to be a decomposition product. A corrected value of 134.6 ppm for  $P(N_3)_3$  was subsequently reported.<sup>2,3</sup> For  $ClP(N_3)_2$  its <sup>31</sup>P chemical shift has been measured not only in the following solvents CH2Cl2, C6H5NO2, and CS2, but also in CH<sub>3</sub>CN where a value of 149.1 ppm was found.<sup>3</sup> The <sup>31</sup>P NMR data have previously been published for  $(C_6H_5)_2NPF_2$  (in CH<sub>3</sub>CN) as 131.0 ppm (triplet) with  ${}^{1}J({}^{31}P-{}^{19}F) = 1239$  Hz, and for  $(C_6H_5)_2NPCl_2$  (without solvent) as 148.0 ppm (singlet).<sup>34</sup> For  $(C_6H_5)_2NPF_2$  its <sup>19</sup>F NMR resonance was also found at -63.7 ppm (doublet) with  ${}^{1}J({}^{19}F-{}^{31}P) = 1241$ Hz.<sup>34</sup>

In the present work, data for  $(C_6H_5)_2NPCl_2$ ,  $(C_6H_5)_2NPF_2$ , and  $(C_6H_5)_2NP(N_3)_2$  were recorded either in  $CD_2Cl_2$ ,  $CDCl_3$ ,  $CD_3CN$ , or  $CH_3CN$  solutions or as neat liquids at variable temperatures. For neat  $(C_6H_5)_2NPCl_2$ , a singlet <sup>31</sup>P resonance

was found with a value of 148.9 ppm, consistent with the published value,<sup>34</sup> whereas in CH<sub>3</sub>CN a singlet at 149.4 ppm was observed. In the case of  $(C_6H_5)_2NPF_2$ , the <sup>31</sup>P NMR spectrum showed a triplet in CD<sub>2</sub>Cl<sub>2</sub> at 131.8 ppm with  ${}^{1}J({}^{31}P-{}^{19}F) = 1237$  Hz, whereas the  ${}^{19}F$  spectrum showed a doublet at -63.3 ppm with  ${}^{1}J({}^{19}F-{}^{31}P) = 1237$  Hz which was again consistent with the literature.<sup>34</sup>

For  $(C_6H_5)_2NP(N_3)_2$ , a singlet <sup>31</sup>P NMR resonance was observed in CD<sub>3</sub>CN at 113.2 ppm. Additionally, three <sup>14</sup>N NMR signals at -144.8, -176.7, and -296.0 ppm were found in CD<sub>3</sub>CN. The first <sup>14</sup>N signal can be attributed to the central N<sub>β</sub> atom in the N<sub>3</sub> group, whereas the second signal is characteristic of the terminal N<sub>γ</sub>, and the third weak, broad signal is due to the N<sub>α</sub> atom bonded to P. These <sup>14</sup>N resonances can be favorably compared with those found in other covalently bonded azido groups to elements such as As  $(-145.3, -175.9, \text{ and } -290 \text{ ppm for As}(N_3)_3)$ ,<sup>35,51</sup> and Sb  $(-136.2, -172.3, \text{ and } -324.5 \text{ ppm for Sb}(N_3)_3)$ .<sup>35</sup> The chemical shift for the N atom in the diphenylamino group was expected to be in the region -330 to -350 ppm<sup>52</sup> but was either too weak and/or too broad to be observed.

The reaction between  $(C_6H_5)_2NPF_2$  and  $(CH_3)_3SiN_3$  with a small amount of CsF as a catalyst in CD<sub>3</sub>CN was followed by <sup>31</sup>P and <sup>19</sup>F NMR spectroscopy in an experiment where the reactants were combined at -196 °C and the temperature was increased gradually inside the NMR spectrometer. In this experiment the formation of  $(C_6H_5)_2NP(N_3)_2$  was first observed at a temperature of -30 °C and slowly increased over 1 h. As expected, the reaction rate to produce  $(C_6H_5)_2NP(N_3)_2$  increased with time and rising temperatures from -20 °C, to 0 °C, and up to 20 °C when decomposition began to be observed. At 25 °C, decomposition products were noticeable as some insoluble material appeared in the bottom of the NMR tube. At the end of the experiment the triplet in the <sup>31</sup>P spectra due to  $(C_6H_5)_2NPF_2$  had completely disappeared while the singlet for  $(C_6H_5)_2NP(N_3)_2$  dominated the spectrum. These results can be seen in Figure 5.

**2.5. Identification of (C\_6H\_5)\_2NPF(N<sub>3</sub>).** During the course of this variable temperature experiment, a new weak doublet in the <sup>31</sup>P spectra gradually grew in at 135.5 ppm with  ${}^{1}J({}^{31}P-{}^{19}F)$ = 1147 Hz. The intensity of this doublet stayed relatively constant over time until the end of the experiment when these resonances disappeared together with the triplet due to  $(C_6H_5)_2$ NPF<sub>2</sub>. The presence of a new doublet can be seen in Figure 6 showing the <sup>31</sup>P NMR spectrum taken after 1 h of reaction at 20 °C. This new species was confirmed in the <sup>19</sup>F NMR spectrum which showed a doublet at -89.2 ppm with a coupling constant  ${}^{1}J({}^{19}F-{}^{31}P) = 1105$  Hz. Given that this new doublet in the <sup>31</sup>P spectrum occurred in the range of those for  $(C_6H_5)_2$ NPF<sub>2</sub> and  $(C_6H_5)_2$ NP $(N_3)_2$  and taken together with its eventual disappearance when all of the  $(C_6H_5)_2NPF_2$  was consumed in its reaction with excess  $(CH_3)_3SiN_3$ , this species can be assigned to the reaction intermediate  $(C_6H_5)_2NPF(N_3)$ . The results of the <sup>31</sup>P and <sup>14</sup>N experiments are combined in Table 2.

## 3. CONCLUSIONS

The novel diazidophosphane,  $(C_6H_5)_2NP(N_3)_2$ , has been synthesized and characterized by its <sup>31</sup>P and <sup>14</sup>N NMR spectra. Furthermore, Raman spectra of the various  $(C_6H_5)_2NPX_2$  (X = F, Cl, N<sub>3</sub>) compounds have all been recorded for the first time with vibrational assignments for these compounds. The



**Figure 5.** Temperature dependent <sup>31</sup>P NMR spectra of the reaction of  $(C_6H_5)_2NPF_2$  with excess  $(CH_3)_3SiN_3$  in CD<sub>3</sub>CN solution in the presence of a catalytic amount of CsF to yield  $(C_6H_5)_2NP(N_3)_2$  at varying temperatures over time. Resonances marked with \* are due to an unstable unidentified decomposition product occurring at temperatures at or above 20 °C.



**Figure 6.** <sup>31</sup>P NMR spectrum of the  $(C_6H_5)_2$ NPF $(N_3)$  intermediate at 20 °C in CD<sub>3</sub>CN upon warm-up from -30 °C from the reaction of  $(C_6H_5)_2$ NPF<sub>2</sub> with excess  $(CH_3)_3$ SiN<sub>3</sub> in the presence of a catalytic amount of CsF. The resonance marked with an asterisk is an unstable unidentified decomposition product which forms at temperatures  $\geq 20$  °C.

intermediate compound  $(C_6H_5)_2NPF(N_3)$  has been shown to be formed in the system of  $(C_6H_5)_2NPF_2$  and excess  $(CH_3)_3SiN_3$  in acetonitrile at low temperatures and has been found to be stable to about 20 °C.

#### 4. EXPERIMENTAL SECTION

**Caution!** The handling of all azides should be done with great respect due to their potentially dangerous properties. All manipulations and reactions should be conducted with appropriate safety measures such as behind shields or barricades in a fume hood with protective clothing such as safety glasses, face shields, leather gloves, and leather suits and ear plugs.

Infrared spectra were recorded on a Midac Model M FTIR spectrometer in the range 4000-400 cm<sup>-1</sup> with samples either as a

compd	$\delta$ $^{31}$ P, ppm	$\delta$ <sup>19</sup> F, ppm	$\delta$ <sup>14</sup> N, ppm	$^{1}J(PF)$ , Hz	ref
PF₃ (neat, −90 °C)	97.0	-34.0		1403	53-56
Me <sub>2</sub> NPF <sub>2</sub> (neat, room temp)	143.0	-65.3		1197	56, 57
PCl <sub>3</sub> (neat, room temp)	219.4				58, 59
$(1,3,5-Me_{3}C_{6}H_{5})P(N_{3})_{2}$ (CH <sub>3</sub> CN)	138				13
$P(N_3)_3$ (CH <sub>3</sub> CN)	134.6				3
$Ph_2NPF_2$ (CH <sub>3</sub> CN)	131.0	-63.7		1239	34
Ph <sub>2</sub> NPCl <sub>2</sub> (neat)	148.0				34
$Ph_2NPF_2$ (CD <sub>3</sub> CN)	131.8	-63.8		1237	this work
Ph <sub>2</sub> NPCl <sub>2</sub> (neat, room temp)	148.9				this work
$Ph_2NPCl_2$ (CD <sub>3</sub> CN)	149.4				this work
$Ph_2NP(N_3)_2$ (CD <sub>3</sub> CN)	113.2		$-144.8 (N_{\beta})$		this work
			$-176.7 (N_{\gamma})$		this work
			$-296.0 (N_{\alpha})$		this work
$Ph_2NPF(N_3)$ (CD <sub>3</sub> CN)	135.5	-89.2		1147	this work

Table 2. Selected Experimental and Literature <sup>31</sup>P and <sup>19</sup>F NMR Values for  $(C_6H_5)_2NPX_2$  (X = Cl, F, N<sub>3</sub>) and Related Compounds

liquid film or a finely ground powder between two AgCl windows in a Barnes Engineering Co. Econo Press. Raman spectra were recorded on a Bruker Equinox 55 FT-RA spectrometer using a Nd:YAG laser at 1064 cm<sup>-1</sup> in the range between 4000 and 80 cm<sup>-1</sup> using either 5 mm o.d. Pyrex J. Young NMR tubes or 9 mm o.d. Teflon-FEP tubes fitted with stainless steel valves as sample containers which were pretreated before use with (CH<sub>3</sub>)<sub>3</sub>SiN<sub>3</sub> and thoroughly pumped out. NMR data for <sup>1</sup>H, <sup>14</sup>N, <sup>19</sup>F, and <sup>31</sup>P were recorded on either a Varian VNMRS-400 or a Varian VNMRS-500 spectrometer, and for <sup>14</sup>N on a Bruker AMX-500 spectrometer. The NMR solvents (CDCl<sub>2</sub> and CD<sub>2</sub>CN) were from Cambridge Isotope Laboratories and were used as received.  $^{1}H$  NMR spectra were referenced to Si(CH<sub>3</sub>)<sub>4</sub>,  $^{14}N$  spectra to  $\text{CH}_3\text{NO}_{23}$   $^{19}\!\bar{\text{F}}$  to  $\text{CFCl}_{33}$  and  $^{31}\text{P}$  to 85%  $\text{H}_3\text{PO}_{4}.$  Geometries and vibrational frequencies and intensities were calculated for three conformers of  $(C_6H_5)_2NP(N_3)_2$  using Gaussian09, Revision A.02, at the B3LYP/6-311+G(p,d) level of theory.<sup>48</sup> The frequency analyses confirmed that all structures were local minima on the potential energy surface with the lowest energy conformer differing by ≤1.6 kcal/mol from the other two.

The phosphorus trichloride (99%) and diphenylamine (99%), both from Sigma-Aldrich, Inc., and triethylamine from Mallinckrodt (OR grade, bp 88-90 °C) were used as received. Sodium fluoride was obtained from Mallinckrodt (Analytical grade) and heated to 650 °C in a stream of  $\text{GN}_2$  (gaseous nitrogen) in order to ensure that it was completely anhydrous, and checked for the absence of NaHF2 and H<sub>2</sub>O by infrared and Raman spectroscopy before being stored in a drybox prior to use. Cesium fluoride was obtained from KBI Chemicals and fused at >700 °C under GN<sub>2</sub> and then finely ground in a drybox. Sodium azide (99.99+%) from Sigma-Aldrich was heated in vacuo at 120 °C overnight to remove any traces of moisture. Benzene (DriSolv) and anhydrous ethyl ether (DriSolv) were both used as received from EMD. Acetonitrile (DriSolv) was either used as received from EMD or was further dried by storage over P2O5. Perdeuterated acetonitrile, CD<sub>3</sub>CN (99.8% D), was obtained from Cambridge Isotope Laboratories and used as an NMR solvent for several <sup>1</sup>H, <sup>14</sup>N, <sup>19</sup>F, and <sup>31</sup>P NMR experiments. Liquid reagents and solvents were transferred to reaction vessels or J. Young NMR tubes inside a GN<sub>2</sub> purged glovebag, or on a Pyrex glass vacuum line using high vacuum or standard Schlenk line techniques. All the other reagents were handled inside the dry N2 atmosphere of a D. L. Herring drybox.

**4.1. Diphenylaminodichlorophosphane**,  $(C_6H_5)_2$ NPCl<sub>2</sub>. In a method similar to that reported in the literature,<sup>34</sup> except with the essential precaution of preventing any water vapor from entering into the reaction apparatus, phosphorus trichloride (26.863 g, 196.61 mmol) and benzene (100 mL) were added inside a GN<sub>2</sub> purged glovebag to a three-necked 500 mL flask. This was followed by the dropwise addition (under a GN<sub>2</sub> atmosphere) of a preformed solution of triethylamine (55 mL, 40 g, 395 mmol), diphenylamine (50 mL,

33.270g, 196.60 mmol), and benzene (150 mL) over 30 min with stirring at room temperature. The mixture was stirred for an additional 17 h, resulting in a golden-brown solution with a white precipitate. This mixture was then refluxed under GN2 at 80 °C for 4.5 h, after which time the solution had turned murky red-brown in color. After the mixture had been cooled to 0 °C overnight and the precipitate had settled out, the liquid phase was separated from the precipitate using GN2-pressurized Schlenk cannula techniques. The volatile benzene and triethylamine were pumped off from the wine-red material at room temperature, resulting in 53.197 g of crude product. Diethyl ether (200 mL) was added to the crude product, and the mixture was cooled to -30 °C which resulted in the appearance of an additional white precipitate. The liquid phase was separated again from the precipitate using GN2-pressurized cannula techniques at -30 °C, and the ether was pumped off, first at -30 °C and then gradually as the mixture was warmed to around 100 °C. Lastly, the mixture was distilled at 130-135 °C in a short-path-length distillation apparatus where the final product was collected at 25 °C as a clear, colorless, viscous liquid. Theoretical mass expected for 196.61 mmol  $(C_6H_5)_2NPCl_2 = 53.104$  g; experimental mass  $(C_6H_5)_2NPCl_2 =$ 39.345 g (yield = 74.1%). Raman spectra and  ${}^{31}P$ ,  ${}^{13}C$ , and  ${}^{1}H$  NMR spectra confirmed the product to be pure  $(C_6H_5)_2NPCl_2$ .

4.2. Diphenylaminodifluorophosphane, (C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>NPF<sub>2</sub>. Diphenylaminodichlorophosphane (15.445 g, 57.18 mmol) was added in the drybox to a 500 mL flask, followed by the addition inside the glovebag of acetonitrile (150 mL) and dried NaF (14.181 g, 337.74 mmol) similar to the literature method<sup>34</sup> except for strict avoidance of moisture. The reaction mixture was then refluxed at 95 °C under a GN<sub>2</sub> atmosphere for 5 h. After cooling the mixture to room temperature, the liquid phase was cannulated using Schlenk techniques under a GN<sub>2</sub> atmosphere into a separate dry 500 mL Pyrex vessel, and the solvent was pumped off at ambient temperature. Finally, the crude product (12.368 g) was distilled in vacuo into a dry short-path-length vacuum distillation apparatus. The crude product was then heated at 45 °C, and a white solid product was collected in a trap at –25 °C under a high vacuum. Upon warming to 20 °C, the solid product melted to a clear colorless liquid having sufficient vapor pressure to allow it to pass through a trap at -6 °C. Theoretical mass expected for 57.18 mmol = 13.562 g; experimental mass of  $(C_6H_5)_2NPF_2 = 11.640$ g (yield = 85.8%). Raman spectra and  ${}^{31}P$ ,  ${}^{19}F$ ,  ${}^{14}N$ ,  ${}^{13}C$ , and  ${}^{1}H$  NMR spectra confirmed the product to be pure (C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>NPF<sub>2</sub>

**4.3. Diphenylaminodiazidophosphane**, ( $C_6H_5)_2NP(N_3)_2$ . Diphenylaminodifluorophosphane (0.534 g, 2.11 mmol) and finely powdered CsF (0.0206 g, 0.135 mmol) as a catalyst were loaded inside the drybox into a preconditioned (with trimethylsilylazide) Teflon ampule equipped with a stainless steel valve. Next, CD<sub>3</sub>CN (approximately 10 mL) was added to the Teflon ampule on the Pyrex vacuum line at -196 °C. After the mixture was warmed to room temperature and the reactants were homogenized, the ampule was

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recooled to -196 °C, and excess trimethylsilylazide (3.538 mmol) was added at -196 °C on the Pyrex vacuum line. The mixture was kept at -30 °C for 2 days with occasional agitation. Raman spectroscopy at -30 °C revealed that the reaction had not gone to completion. Eventually, the temperature was raised to 0 °C, then briefly to 20 °C, and then to 25 °C until there was no more evidence via <sup>31</sup>P NMR spectroscopy of any remaining diphenylaminodifluorophosphane. The liquid products from the reaction mixture were cannulated from the insoluble CsF catalyst into a separate Teflon ampule at -30 °C, after which the excess trimethylsilylazide and the solvent were pumped off between -30 and -20 °C resulting in a clear, viscous/semisolid material. Raman spectra of the final product showed only bands due to  $(C_6H_5)_2NP(N_3)_2$ .

## ASSOCIATED CONTENT

## **S** Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorg-chem.5b02097.

Tables of Raman data, XYZ coordinates, and bond lengths and angles (PDF)

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#### Notes

The authors declare no competing financial interest.

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## DEDICATION

In memory of Prof. Dr. Reinhard Schmutzler.

#### REFERENCES

- (1) Buder, W.; Schmidt, A. Z. Anorg. Allg. Chem. 1975, 415, 263–267.
- (2) Dillon, K. B.; Platt, A. W. G.; Waddington, T. C. Inorg. Nucl. Chem. Lett. 1978, 14, 511-513.
- (3) Dillon, K. B.; Platt, A. W. G.; Waddington, T. C. J. Chem. Soc., Dalton Trans. 1980, 1036–1041.
- (4) Zeng, X.; Wang, W.; Liu, F.; Ge, M.; Sun, Z.; Wang, D. Eur. J. Inorg. Chem. 2006, 2006, 416–421.
- (5) Wang, L.; Warburton, P. L.; Mezey, P. G. J. Phys. Chem. A 2005, 109, 1125–1130.
- (6) Klapötke, T. M.; Schulz, A. Main Group Metal Chemistry 1997, 20, 325–338.
- (7) Schulz, A.; Villinger, A. Chem. Eur. J. 2012, 18, 2902-2911.
- (8) Tesi, G.; Haber, C. P.; Douglas, C. M. Proc. Chem. Soc. (London) 1960, 219–220.
- (9) Paciorek, K. L.; Kratzer, R. Inorg. Chem. 1964, 3, 594-595.
- (10) O'Neill, S. R.; Shreeve, J. M. Inorg. Chem. 1972, 11, 1629-1631.
- (11) Chevrier, P. J.; Brownstein, S. J. Inorg. Nucl. Chem. 1980, 42, 1397-1405.

- (12) Hering, C.; Schulz, A.; Villinger, A. Angew. Chem., Int. Ed. 2012, 51, 6241-6245.
- (13) Cowley, A. H.; Gabbai, F.; Schluter, R.; Atwood, D. J. Am. Chem. Soc. **1992**, 114, 3142–3144.
- (14) Weigand, J. J.; Feldmann, K. O.; Henne, F. D. J. Am. Chem. Soc. 2010, 132, 16321-16323.
- (15) Henne, F. D.; Dickschat, A. T.; Hennersdorf, F.; Feldmann, K. O.; Weigand, J. J. Inorg. Chem. **2015**, *54*, 6849–6861.
- (16) Volgnandt, P.; Schmidt, A. Z. Anorg. Allg. Chem. 1976, 425, 189-192.
- (17) Dillon, K. B.; Platt, A. W. G.; Waddington, T. C. J. Chem. Soc., Dalton Trans. 1981, 2292–2295.
- (18) Roesky, H. W. Angew. Chem., Int. Ed. Engl. 1967, 6, 637.
- (19) Haiges, R.; Schneider, S.; Schroer, T.; Christe, K. O. Angew. Chem., Int. Ed. 2004, 43, 4919–4924.
- (20) Portius, R.; Fowler, P. W.; Adams, H.; Todorova, T. Z. Inorg. Chem. 2008, 47, 12004–12009.
- (21) Dillon, K. B.; Platt, A. W. G.; Waddington, T. C. J. Chem. Soc., Chem. Commun. 1979, 889.
- (22) Dillon, K. B.; Platt, A. W. G. J. Chem. Soc., Dalton Trans. 1983, 1159–1164.
- (23) Schmidt, A. Chem. Ber. 1970, 103, 3923-3927.
- (24) Bruder, W.; Schmidt, A. Chem. Ber. 1973, 106, 3812-3816.
- (25) Zeng, X.; Bernhardt, E.; Beckers, H.; Willner, H. Inorg. Chem. 2011, 50, 11235-11241.
- (26) Li, D.; Li, H.; Zhu, B.; Zeng, X.; Willner, H.; Beckers, H.; Neuhaus, P.; Grote, D.; Sander, W. *Phys. Chem. Chem. Phys.* **2015**, *17*, 6433–6439.
- (27) Götz, N.; Herler, S.; Mayer, P.; Schulz, A.; Villinger, A.; Weigand, J. J. *Eur. J. Inorg. Chem.* **2006**, 2006, 2051–2057.
- (28) Aubauer, C.; Klapötke, T. M.; Nöth, H.; Schulz, A.; Suter, M.; Weigand, J. Chem. Commun. 2000, 2491–2492.
- (29) Aubauer, C.; Karaghiosoff, K.; Klapötke, T. M.; Kramer, G.; Schulz, A. Z. Anorg. Allg. Chem. **2001**, 627, 2547–2552.
- (30) Muralidharan, K.; Omotowa, B. A.; Twamley, B.; Piekarski, C.; Shreeve, J. M. Chem. Commun. 2005, 5193–5195.
- (31) Haiges, R.; Rahm, M.; Dixon, D. A.; Garner, E. B., III; Christe, K. O. Inorg. Chem. **2012**, *51*, 1127–1141.
- (32) Haiges, R.; Rahm, M.; Christe, K. O. Inorg. Chem. 2013, 52, 402-414.
- (33) JANAF Themochemical Tables; Vol. 5, N<sub>3</sub>(g), 12-31-1970.
- (34) Falius, H.; Babin, M. Z. Anorg. Allg. Chem. 1976, 420, 65-73.
- (35) Haiges, R.; Vij, A.; Boatz, J. A.; Schneider, S.; Schroer, T.; Gerken, M.; Christe, K. O. *Chem. - Eur. J.* **2004**, *10*, 508–517.
- (36) Yost, D. M.; Anderson, T. F. J. Chem. Phys. 1934, 2, 624-627.
- (37) Wilson, M. K.; Polo, S. R. J. Chem. Phys. 1952, 20, 1716-1719.
- (38) Clark, R. J. H.; Rippon, D. M. J. Mol. Spectrosc. 1974, 52, 58-71.
- (39) Müller, A.; Niecke, E.; Krebs, B.; Glemser, O. Z. Naturforsch., B:
- J. Chem. Sci. 1968, 23B, 588-594.
- (40) Müller, A.; Königer, F.; Cyvin, S. J.; Fadini, A. Spectrochim. Acta 1973, 29A, 219–228.
- (41) Dean, C. R. S.; Finch, A.; Gates, P. N. J. Chem. Soc., Dalton Trans. 1972, 1384–1387.
- (42) Burdett, J. K.; Hodges, L.; Dunning, V.; Current, J. H. J. Phys. Chem. 1970, 74, 4053–4059.
- (43) Delwaulle, M. L.; Francois, F. J. Chim. Physique 1949, 46, 87–97.
- (44) Davis, P. W.; Oetjen, R. A. J. Mol. Spectrosc. 1958, 2, 253–258.
  (45) Müller, A.; Niecke, E.; Glemser, O. Z. Anorg. Allg. Chem. 1967,
- 350, 256–262.
- (46) Andrews, L.; Frederick, D. L. J. Phys. Chem. 1969, 73, 2774–2778.
- (47) Weidlein, J.; Müller, U.; Dehnicke, K. Schwingungsspektroskopie, Eine Einführung; Georg Thieme Verlag: Stuttgart, 1982; pp 52–54.
- (48) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima,

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T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A., Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. *Gaussian 09, Revision A.02*; Gaussian, Inc.: Wallingford, CT, 2009.

(49) Morris, E. D., Jr; Nordman, C. E. Inorg. Chem. 1969, 8, 1673–1676.

(50) Mitzel, N. W. J. Chem. Soc., Dalton Trans. 1998, 3239-3242.

(51) Geissler, P.; Klapötke, T. M.; Kroth, H.-J. Spectrochim. Acta, Part A **1995**, *51A*, 1075–1078.

(52) Witanowski, M.; Stefaniak, L.; Webb, G. A. Annual Reports on NMR Spectroscopy; Webb, G. A., Ed.;Academic Press: London, 1992; pp 113, 124, and 131.

(53) Gutowsky, H. S.; McCall, D. W.; Slichter, C. P. J. Chem. Phys. 1953, 21, 279–292.

(54) Gutowsky, H. S.; McCall, D. W. J. Chem. Phys. 1954, 22, 162–164.

(55) Holmes, R. R.; Gallagher, W. P. Inorg. Chem. 1963, 2, 433–437.
(56) Reddy, G. S.; Schmutzler, R. Z. Naturforsch., B: J. Chem. Sci. 1965, 20b, 104–109.

(57) Schmutzler, R. Inorg. Chem. 1964, 3, 415-421.

(58) Muller, N.; Lauterbur, P. C.; Goldenson, J. J. Am. Chem. Soc. 1956, 78, 3557–3561.

(59) Van Wazer, J. R.; Callis, C. F.; Shoolery, J. N.; Jones, R. C. J. Am. Chem. Soc. **1956**, 78, 5715–5726.