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Reactions of a *P*-chloro-iminophosphane with Main Group Nucleophiles: Syntheses and X-ray Crystal Structure Analyses of Two 1,3-Diphosphatetraz-3-ene Derivatives

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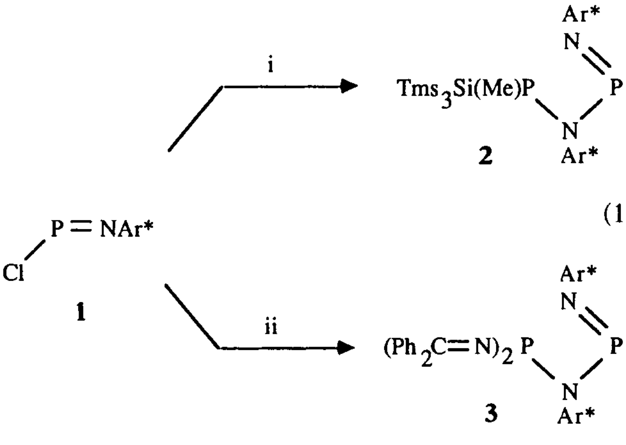
ABSTRACT

*The reactions of chloro(2,4,6-tri-*tert*-butylphenyliminο)phosphane with lithium tris(trimethylsilyl)silanide and lithium diphenylketimide furnish products resulting from the incorporation of a second chloroiminophosphane molecule into the primary substitution product and subsequent nucleophilic displacement of the chlorine ligand. The final products have been characterized by X-ray structure analyses, which revealed some remarkable features.*

RESULTS AND DISCUSSION

In the last few years iminophosphanes have developed into valuable building blocks in organoelement chemistry due to the multi-faceted chemical behavior of this class of compounds. Among these, iminophosphanes bearing a nucleofugic leaving group on phosphorus are still attracting a great deal of interest. These are able to undergo ligand displacement reactions with nucleophiles leaving the double bond system intact [1]. However, only the recent discovery of stable *P*-halogeno [2] and *P*-aryloxy [3] derivatives did succeed in enhancing considerably the applicability of substitution reactions for the syntheses of new iminophosphanes. In particular, the chloroiminophosphane Cl–P=NAr* **1** (Ar* = 2,4,6-(t-Bu)$_3$C$_6$H$_2$) turned out to play a key role for the generation of a variety of novel P-functionalized phosphorus–nitrogen double bond systems.

Bearing this in mind we conducted experiments with the aim of *inter alia* generating derivatives containing the PN–π system in conjugation with further double bonds and systems containing *P*-silyl functions. However, as became clear after spectroscopic investigations, the reactions with the lithiated diphenylketimine and with LiSiTms$_3$ (Tms = SiMe$_3$) did not produce the desired target molecules but instead compounds **2** and **3** (Equation 1). The products obtained consisted of two PN moieties, thus belonging to the class of 1,3-diphosphatetraz-



(1)

Dedicated to Professor Ekkehard Fluck on the occasion of his sixtieth birthday.

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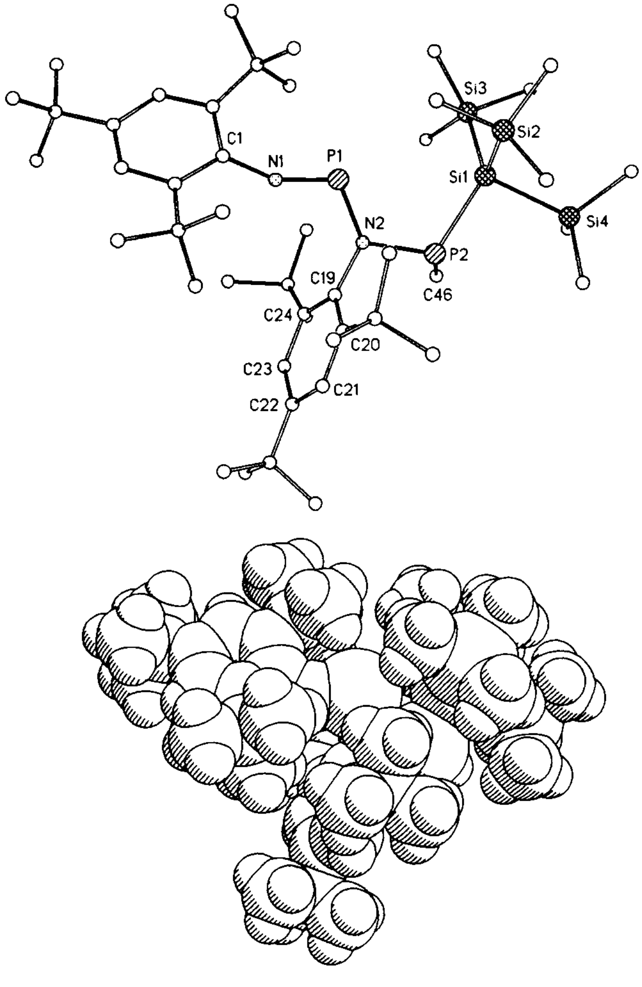
3-enes, as established by two X-ray diffraction studies. This was especially surprising in the case of the reaction producing **3**, since treatment of **1** with lithium di-*tert*-butylketimide or lithium 9-fluorenylideneketimide furnished the stable mono-substituted iminophosphanes in their trans- and cis-configuration, respectively [4].

The silyl reagent had been chosen with regard to the steric demand of the tris(trimethylsilyl)silyl ligand, which was thought to impart kinetic stability to the desired silyliminophosphane. The in situ preparation of $LiSiTms_3$ from tetrakis(trimethylsilyl)silane and methyllithium accounts for the product of the above reaction containing a methyl substituent in the phosphane moiety. However, reactions starting from the purified silanide also furnished the same product, though in much lower yields. Compound **2** was the sole compound obtainable as suitable single crystals.

The crystal structure determination of the aminoiminophosphane **2** (Figure 1) revealed some quite interesting peculiarities.

FIGURE 1 Ball-and-Stick and Space-Filling Representation of Aminoiminophosphane **2**



The sterically highly demanding substituents at the amino- as well as at the iminonitrogen lead to extreme steric crowding around the PN double bond system. This steric crowding is responsible for some remarkable features of this trans-configurated aminoiminophosphane documented in the structural parameters of **2**. Some important bond lengths and angles are presented in Table 1.

The relatively short phosphorus–nitrogen distance of 153.7(3) pm is characteristic of the lower region of double bond lengths found from trans-aminoiminophosphanes [1], whereas the very large N2–P1–N1–C1 torsion angle (−153.6(4)°) clearly demonstrates the considerable distortion of this double bond. This, as well as the strongly widened valence angle at the iminonitrogen (152.3(4)°) has to be attributed to the presence of the extremely bulky substituents.

Compound **2** constitutes the first example of an aryl-substituted iminophosphane where the terminal arene π-system (C1–C18) is not arranged orthogonally with respect to the double bond π-system. The former has been rotated out of the N2–P1–N1–C1 plane by about 40°, which is why a conjugative interaction of the arene π system with the p_π–p_π system of the PN double bond has to be taken into consideration. Comparing the N1–C1 and N2–C19 distances (139.7(5) and 145.8(5) pm, respectively) one can easily discern the distinct shortening of the nitrogen–carbon bond length of the imino-2,4,6-tri-*tert*-butylphenyl group. The valence angles at the nitrogen atoms indicate an essentially sp^2-hybridized aminonitrogen, whereas sp character can be attributed to the nitrogen atom of the P=N system. The arrangement of the amino substituents coplanar to the N2–P1–N1–C1 plane is a common feature of all aminoiminophosphanes crystallographically investigated so far. However, the angle between the P2–N2–P1 plane and the plane determined by C19–C24 (72°) imposed on the molecule by repulsive ligand interactions should be noted.

The environment around the phosphane–phosphorus is pyramidal, and its lone pair makes an angle of 35° with the lone pair of the amino nitrogen N2. The iminophosphane and the silyl ligands show a cis arrangement with respect to the P2–N2 axis. This P2–N2 bond (179.1(3) pm) appears to be considerably lengthened compared with an average phosphorus–nitrogen single bond (170 pm), which is in accord with a weak, highly polar PN linkage. Due to its σ-donor and π-acceptor properties the tris(trimethylsilyl)silyl ligand is capable of favorably influencing this bonding situation, where the N2 atom is assigned a partial negative charge, the P2 atom a partial positive charge. Furthermore, the P2–Si1 distance is somewhat longer than usual, which is again due to steric crowding; the nonbonding P1–Si1 distance amounts to 360.2(2) pm.

TABLE 1 Important Bond Lengths (pm) and Angles (degrees) for the Aminoiminophosphane **2**

P(1)–N(1)	153.7(3)	P(1)–N(2)	168.1(3)
P(2)–N(2)	179.1(3)	P(2)–Si(1)	229.2(2)
P(2)–C(46)	184.0(3)	N(1)–C(1)	139.7(5)
N(2)–C(19)	145.8(5)	Si(1)–Si(2)	236.9(1)
Si(1)–Si(3)	237.5(3)	Si(1)–Si(4)	238.5(2)
P(1) · · · Si(1)	360.2(2)		
N(1)–P(1)–N(2)	111.2(2)	N(2)–P(2)–Si(1)	112.9(1)
N(2)–P(2)–C(46)	102.3(2)	Si(1)–P(2)–C(46)	102.4(2)
P(1)–N(1)–C(1)	152.3(4)	P(1)–N(2)–P(2)	120.6(2)
P(1)–N(2)–C(19)	129.9(2)	P(2)–N(2)–C(19)	108.8(3)
P(2)–Si(1)–Si(2)	112.3(1)	P(2)–Si(1)–Si(3)	123.1(1)
Si(2)–Si(1)–Si(3)	110.3(1)	P(2)–Si(1)–Si(4)	96.3(1)
Si(2)–Si(1)–Si(4)	105.8(1)	Si(3)–Si(1)–Si(4)	106.5(1)
N(2)–P(1)–N(1)–C(1)	−153.6(4)	N(1)–P(1)–N(2)–P(2)	−172.5(2)
N(1)–P(1)–N(2)–C(19)	−3.1(3)	Si(1)–P(2)–N(2)–P(1)	−4.7(2)
Si(1)–P(2)–N(2)–C(19)	−176.2(2)	C(46)–P(2)–N(2)–P(1)	−114.1(3)
C(46)–P(2)–N(2)–C(19)	74.5(3)	P(1)–N(1)–C(1)–C(2)	7.4(5)
P(1)–N(1)–C(1)–C(6)	−175.4(3)		

The P2 valence angle as well as the widened angle at the imino nitrogen atom are also attributed to the voluminous $SiTms_3$ group. Thus a repulsive interaction between the silyl substituent and the P1 lone pair must be taken into account. This is demonstrated by the relatively large N2–P1–N1 angle (111.2(2)°). Moreover, the P1–N2–C19 angle, widened to 129.9(2)°, together with the smaller P2–N2–C19 angle (108.8(3)°), are accounted for by repulsion of the N2 aryl ligand and the N1 lone pair. For the Si1 atom a distorted tetrahedral coordination sphere was found (P2–Si1–Si3 123.1(1)°, P2–Si1–Si4 96.3(1)°), with this distortion being brought about by steric effects involving the lone pairs of P1 and P2. These effects are also responsible for the nondetectable phosphorus–phosphorus coupling of the ^{31}P resonances (δ = 334.0 ppm, 32.9 ppm), which is why a binuclear species had a priori not been thought of. However, the considerable influence of sterically demanding substituents on the spatial orientation of lone pairs, and thus on the spin–spin coupling constants of magnetically active nuclei, is well documented [5]. Thus, because of the molecular structure of **2**, the lacking coupling was readily explained by the special structural features discussed above. Furthermore, the appearance of a quartet in the high field region of the proton coupled phosphorus spectrum ($^2J_{HP}$ = 7 Hz), as well as the hindered rotation of the aryl ligands, inferred from the ^{1}H-NMR spectra, could be explained on the basis of the results obtained.

The formation of compounds **2** and **3** can be envisaged to proceed according to Equation 2. Thus, the mono-substitution product is postulated to be an intermediate incorporating another chloroiminophosphane molecule, which can be viewed as a formal 1,2-addition of $[Cl^- \ {}^+PNAr^*]$ **1** to the substituted P=N system. Nucleophilic displacement of the chlorine ligand then furnishes the respective final products.

The skeletal features of the 1,3-diphosphatetraz-3-ene **3** are rather similar to those observed for **2**. There are, however, a few noteworthy deviations (cf. Table 2). In total, as can be seen from Figure 2, compound **3** appears to be less sterically crowded than **2**, though not by much. The P=N bond length is virtually identical (153.9(6) pm) with that in **2**, but, in stark contrast, the valence angle at the iminophosphane–nitrogen is found here to be 135.2(5)°. This establishes an essentially sp^2-hybridized nitrogen atom, and together with the nondistortion of the double bond system (N2–P1–N1–C1 178.6(6)°; (cf. **2**: −153.6(4)°)) this is clearly related to the presence of less bulky substituents. As a consequence

$$\begin{tikzcd}
\mathbf{1} + \text{LiR} \arrow[r, "-\text{LiCl}"'] & {\left[\text{R}-\text{P}=\text{NAr}^*\right]} \arrow[r, "+\mathbf{1}"] & {\left[\text{RP(Cl)}-\text{NAr}^*-\text{P}=\text{NAr}^*\right]} \arrow[d, "\text{LiR}"', "-\text{LiCl}"] \\
 & & \mathbf{2},\ \mathbf{3}
\end{tikzcd} \tag{2}$$

$R = Me/Tms_3Si, Ph_2C=N$

FIGURE 2 Ball-and-Stick and Space-Filling Representation of Aminoiminophosphane **3**

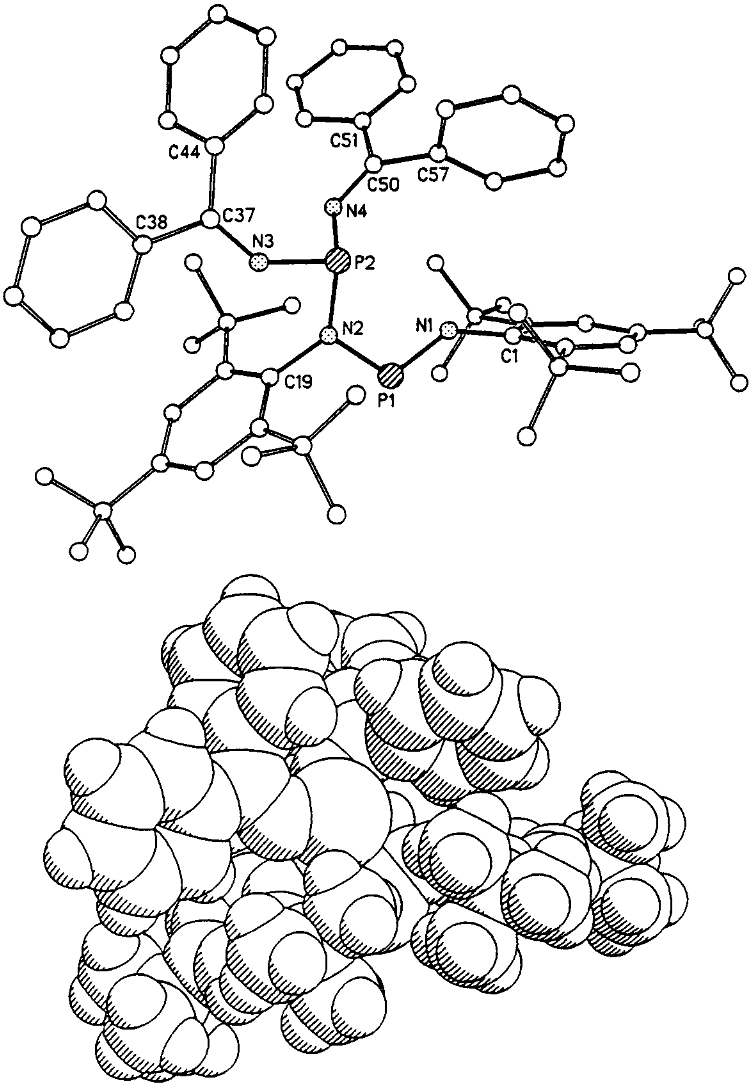


TABLE 2 Important Bond Lengths (pm) and Angles (degrees) for the Aminoiminophosphane **3**

P(1)–N(1)	153.9(6)	P(1)–N(2)	168.8(5)
N(1)–C(1)	143.7(8)	N(2)–C(19)	147.8(9)
N(2)–P(2)	178.5(6)	P(2)–N(3)	169.3(5)
P(2)–N(4)	174.1(7)	N(3)–C(37)	128.3(9)
C(37)–C(38)	149.4(10)	C(37)–C(44)	149.5(12)
N(4)–C(50)	126.2(10)	C(50)–C(51)	146.3(12)
C(50)–C(57)	152.8(11)		
N(1)–P(1)–N(2)	107.4(3)	P(1)–N(1)–C(1)	135.2(5)
P(1)–N(2)–C(19)	110.1(4)	P(1)–N(2)–P(2)	122.7(3)
C(19)–N(2)–P(2)	125.4(4)	N(2)–P(2)–N(3)	94.2(3)
N(2)–P(2)–N(4)	101.7(3)	N(3)–P(2)–N(4)	104.6(3)
P(2)–N(3)–C(37)	136.4(6)	N(3)–C(37)–C(38)	116.7(7)
N(3)–C(37)–C(44)	125.7(7)	C(38)–C(37)–C(44)	117.6(6)
P(2)–N(4)–C(50)	123.3(5)	N(4)–C(50)–C(51)	119.5(7)
N(4)–C(50)–C(57)	125.6(7)	C(51)–C(50)–C(57)	114.8(7)
N(2)–P(1)–N(1)–C(1)	178.6(6)		

the N1–C1 bond distance is now of average size (143.7(8) pm (cf. **2**: 139.7(5) pm) and the N2–P1–N1 angle is slightly decreased (107.4(3)° vs. 111.2(2)° in **2**). This ability of nitrogen to adapt to different steric (and electronic) situations can be understood in terms of isovalent hybridization [6] shown by first row main group elements.

As in **2** the P2–N2 distance of 178.5(6) pm again is considerably longer than an average phosphorus–nitrogen single bond with the N2 atom also being sp^2 hybridized. Compound **3** can formally be viewed as the combination of a diaminophosphenium cation, a species well established in low coordinate phosphorus chemistry [7], and a diaza-2-phospha-allylanion, although this interpretation should not be overemphasized. The pyramidalization of P2 is more distinct due to the absence of π-acceptor ligands (sum of angles 300.5° vs. 317.6° in **2**). The distortion of the P2 environment together with the widened P2–N4 bond distance (174.1(7) pm) allow minimization of steric interactions in the arrangement of the ketimine ligands. The carbon and nitrogen atoms of the latter (N3═C37, N4═C50) show the sp^2 hybridization anticipated, and do not merit special mention.

EXPERIMENTAL

All manipulations were carried out under a dry, oxgyen-free argon atmosphere, with all solvents dried and distilled under argon prior to use. NMR spectra were recorded on a multinuclear spectrometer at 90 (^{1}H), 20 (^{13}C), and 32 MHz (^{31}P) with TMS as internal standard (^{1}H, ^{13}C) and 85% H_3PO_4 (^{31}P) as external standard.

Preparation of Tms$_3$Si(Me)P–NAr–P═NAr* **2***

A precooled solution of 1.63 g Cl–P═NAr* **1** (Ar* = 2,4,6-(*t*-Bu)$_3C_6H_2$) (5 mmol) in 10 mL of THF was added at −78°C to a solution of LiSiTms$_3$ (prepared in situ according to [8], 5 mmol) in 10 mL of THF. After having been warmed to ca. 10°C within 4 h the solvent was removed in vacuo, and the residue was suspended in 20 mL of pentane and filtered. The filtrate was then reduced to ca. 5 mL and left to crystallize at 3°C. After 4 d **2** was obtained as yellow crystals in 22% yield (0.83 g). ^{31}P-{^{1}H}-NMR (pentane/C_6D_6) δ = 334.0, 32.9; ^{31}P-NMR δ = 334.0 (s), 32.9 (q, J_{PH} 7 Hz); ^{1}H-NMR (C_6D_6) δ = 7.6 (m, 4H, Ar*); 2.4 (d, 7 Hz, 3H, PMe); 2.1 (s, 9H, CMe3); 1.7 (s, 18H, CMe$_3$); 1.6 (s, 9H, CMe$_3$); 1.5 (s, 9H, CMe$_3$); 1.4 (s, 9H, CMe$_3$); 0.6 (s, 27H, Si(SiMe)$_3$)$_3$).

Anal. Calcd. for $C_{46}H_{88}N_2P_2Si_4$: C, 65.55; H, 10.45; N, 332. Found: C, 65.15; H, 10.65; N 3.6.

TABLE 3 Atomic Coordinates (× 10^4) and Equivalent Isotropic Displacement Parameters (pm^2 × 10^{-1}) for the Aminoiminophosphane **2**

	x	*y*	*z*	*U(eq)*[a]
P(1)	0	3190(1)	0	33(1)
P(2)	−1197(1)	2135(1)	−516(1)	37(1)
N(1)	323(1)	4167(2)	283(2)	37(2)
N(2)	−757(1)	3202(2)	−292(2)	31(2)
Si(1)	−663(1)	852(1)	−476(1)	38(1)
Si(2)	319(1)	415(1)	1066(1)	52(1)
Si(3)	−462(1)	662(1)	−1481(1)	52(1)
Si(4)	−1529(1)	−245(1)	−974(1)	67(1)
C(1)	748(2)	4843(2)	386(2)	34(2)
C(2)	1076(2)	4733(2)	46(2)	34(2)
C(3)	1326(2)	5527(2)	−53(2)	41(2)
C(4)	1335(2)	6400(2)	244(2)	39(2)
C(5)	1110(2)	6459(2)	707(2)	41(2)
C(6)	841(2)	5715(2)	823(2)	37(2)
C(7)	1192(2)	3781(2)	−214(2)	40(2)
C(8)	1500(2)	3078(2)	580(2)	48(2)
C(9)	1722(2)	3863(3)	−302(3)	58(3)
C(10)	535(2)	3418(2)	−1160(2)	47(2)
C(11)	1597(2)	7271(2)	104(3)	53(3)
C(12)	2190(3)	7692(3)	1051(3)	93(4)
C(13)	1011(3)	7983(3)	−488(3)	78(4)
C(14)	1831(3)	7056(3)	−409(4)	79(4)
C(15)	691(2)	5853(2)	1452(2)	45(2)
C(16)	981(2)	5017(3)	2127(3)	63(3)
C(17)	−70(2)	5986(3)	871(3)	66(3)
C(18)	1053(2)	6720(3)	2074(3)	68(3)
C(19)	−1107(1)	3965(2)	−269(2)	30(2)
C(20)	−1092(2)	4013(2)	474(2)	32(2)
C(21)	−1515(2)	4654(2)	398(2)	38(2)
C(22)	−1920(2)	5298(2)	−328(2)	41(2)
C(23)	−1880(2)	5263(2)	−993(2)	41(2)
C(24)	−1501(2)	4615(2)	−1012(2)	34(2)
C(25)	−662(2)	3424(2)	1397(2)	36(2)
C(26)	−314(2)	4106(2)	2233(2)	49(2)
C(27)	−1141(2)	2784(3)	1357(3)	55(3)
C(28)	−72(2)	2837(2)	1656(2)	44(2)
C(29)	−2355(2)	6008(3)	−347(3)	58(3)
C(30)	−1870(3)	6666(3)	491(3)	103(4)
C(31)	−2798(3)	6585(4)	−1216(3)	102(4)
C(32)	−2789(3)	5522(4)	−219(5)	113(5)
C(33)	−1571(2)	4763(2)	−1871(2)	46(2)
C(34)	−1293(3)	5750(3)	−1783(3)	72(4)
C(35)	−1194(2)	4105(3)	−2006(3)	64(3)
C(36)	−2331(2)	4714(3)	−2770(2)	64(3)
C(37)	1047(2)	1271(3)	1732(3)	67(3)
C(38)	659(3)	−680(3)	973(3)	81(4)
C(39)	84(3)	155(4)	1760(3)	87(4)
C(40)	−984(3)	1475(3)	−2499(3)	86(4)
C(41)	456(2)	844(3)	−831(3)	72(4)
C(42)	−671(3)	−561(3)	−1947(4)	84(4)
C(43)	−1908(3)	19(4)	−468(4)	96(5)
C(44)	−2228(2)	−264(4)	−2274(4)	98(4)
C(45)	−1163(3)	−1463(3)	−592(5)	114(6)
C(46)	−1967(2)	2236(3)	−1765(3)	64(3)

[a] Equivalent isotropic *U* defined as one third of the trace of the orthogonalized U_{ij} tensor.

TABLE 4 Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (pm^2 × 10^{-1}) for the Aminoiminophosphane **3**

	x	*y*	*z*	*U*(*eq*)^a
P(1)	2793(1)	3348(1)	2783(1)	47(1)
N(1)	3789(4)	3590(3)	2741(3)	44(2)
C(1)	4729(5)	3685(4)	3205(3)	44(3)
C(2)	5027(5)	4342(4)	3456(3)	49(3)
C(3)	6000(6)	4408(5)	3853(4)	62(3)
C(4)	6649(5)	3878(5)	4008(4)	62(3)
C(5)	6316(5)	3245(4)	3762(4)	57(3)
C(6)	5370(5)	3116(4)	3365(3)	51(3)
C(7)	4362(6)	4984(4)	3353(4)	63(4)
C(8)	3893(6)	5143(4)	2619(3)	65(4)
C(9)	3610(6)	4875(4)	3724(4)	76(4)
C(10)	4919(6)	5647(4)	3644(5)	97(5)
C(11)	7699(6)	4018(6)	4435(5)	85(4)
C(12)	8230(9)	3367(9)	4631(10)	298(14)
C(13)	7716(8)	4359(12)	5023(8)	326(17)
C(14)	8228(8)	4389(11)	4075(7)	264(14)
C(15)	5103(5)	2358(4)	3153(4)	57(3)
C(16)	4773(5)	2295(4)	2396(4)	68(4)
C(17)	4349(5)	2087(4)	3472(4)	64(4)
C(18)	5986(6)	1872(4)	3400(5)	89(4)
N(2)	2015(3)	3393(3)	2016(2)	40(2)
C(19)	1042(5)	3159(4)	2022(3)	43(3)
C(20)	739(5)	2472(4)	1829(3)	48(3)
C(21)	−176(5)	2282(4)	1881(4)	57(3)
C(22)	−761(5)	2683(5)	2125(3)	54(3)
C(23)	−429(5)	3338(5)	2312(4)	60(3)
C(24)	433(5)	3601(4)	2255(4)	52(3)
C(25)	1261(5)	1924(4)	1544(4)	56(3)
C(26)	2383(5)	1893(4)	1842(4)	64(3)
C(27)	1032(5)	2028(4)	787(4)	71(4)
C(28)	933(6)	1187(4)	1651(5)	92(5)
C(29)	−1718(5)	2414(5)	2207(4)	68(4)
C(30)	−2418(6)	2972(6)	2244(6)	135(7)
C(31)	−2228(8)	1932(7)	1640(6)	175(9)
C(32)	−1474(7)	1983(7)	2834(6)	162(8)
C(33)	589(5)	4370(4)	2468(4)	62(4)
C(34)	1390(6)	4773(4)	2317(4)	71(4)
C(35)	−340(6)	4784(5)	2119(6)	121(6)
C(36)	730(7)	4404(5)	3212(5)	106(5)
P(2)	2277(1)	3861(1)	1364(1)	46(1)
N(3)	1113(4)	3867(3)	883(3)	53(3)
C(37)	673(5)	3823(4)	264(4)	57(3)
C(38)	−407(5)	3875(4)	66(4)	55(3)
C(39)	−910(6)	4145(4)	−553(4)	68(4)
C(40)	−1902(7)	4215(5)	−718(5)	84(4)
C(41)	−2392(6)	4049(5)	−280(5)	85(4)
C(42)	−1909(6)	3772(5)	325(5)	90(5)
C(43)	−902(6)	3698(5)	501(4)	74(4)
C(44)	1145(6)	3711(5)	−269(4)	61(4)
C(45)	869(7)	3151(5)	−686(4)	89(5)
C(46)	1274(10)	3053(8)	−1192(6)	128(7)
C(47)	1950(9)	3501(10)	−1281(6)	142(9)
C(48)	2213(7)	4070(8)	−875(6)	132(7)
C(49)	1800(6)	4162(6)	−367(4)	87(5)
N(4)	2839(4)	3235(3)	1015(3)	48(2)
C(50)	3647(6)	3324(4)	908(3)	52(3)
C(51)	4022(5)	2795(4)	556(4)	53(3)
C(52)	4970(6)	2765(5)	532(4)	76(4)
C(53)	5300(7)	2259(6)	205(5)	94(5)
C(54)	4686(8)	1757(6)	−116(4)	82(5)
C(55)	3732(8)	1765(5)	−100(5)	85(5)
C(56)	3397(7)	2274(5)	223(4)	75(4)
C(57)	4300(6)	3953(4)	1114(4)	63(4)
C(58)	5032(7)	3962(6)	1707(5)	97(5)
C(59)	5720(8)	4495(7)	1888(6)	112(6)
C(60)	5649(9)	5015(7)	1465(8)	128(8)
C(61)	4944(9)	5042(7)	896(9)	163(9)
C(62)	4268(8)	4497(6)	710(7)	142(7)

[a] Equivalent isotropic *U* defined as one third of the trace of the orthogonalized U_{ij} tensor

Preparation of $(Ph_2C{=}N)_2P{-}NAr^*{-}P{=}NAr^*$ **3**

A solution of $LiNCPh_2$ (prepared in situ according to [9], 6 mmol) in 15 mL of THF was added at −78°C very slowly to a solution of 1.96 g $Cl{-}P{=}NAr^*$ **1** (6 mmol) in 15 mL of Et_2O. After 3 h the reaction mixture was warmed to ambient temperature, evaporated to dryness, and the residue taken up in 30 mL of pentane. Insoluble material was removed by filtration, and the filtrate reduced in volume. Compound **3** could be isolated as an orange crystalline solid in 44% yield (2.10 g). $^{31}P\{^1H\}$-NMR (pentane/C_6D_6) $\delta = 296.6, 106.0$ (J_{PP} 6 Hz); ^1H-NMR (C_6D_6) $\delta = 7.55$–6.94 (m, 24H, Ph/Ar*), 1.90–1.24 (m, 54H, CMe_3); $^{13}C\{^1H\}$-NMR (C_6D_6) $\delta = 175.3$ (d, J_{PC} 22 Hz, N=C), 141.6–121.7 (m, Ph/Ar*), 39.3–25.7 (m, Ar*).

Anal. Calcd. for $C_{62}H_{78}N_4P_2$: C, 79.11; H, 8.35; N, 5.95. Found: C, 78.97; H, 8.55; N, 6.48.

X-RAY STRUCTURE DETERMINATIONS

Single crystals of **2** and **3** were obtained by low temperature crystallization from Et_2O/pentane (1:3) and pentane, respectively. The data were collected at ambient temperatures on a Nicolet R3m four-circle diffractometer (ω-scan mode, MoK_α radiation, $\lambda = 71.073$ pm) and solved and refined with SHELXTL and SHELXTL-Plus, respectively.

Compound **2** [**3**], $C_{46}H_{88}N_2Si_4P_2$ [$C_{62}H_{78}N_4P_2$], $M_r = 843.5$ [941.2], crystallizes in space group *Cc* (No. 9) [$P2_1/c$ (No. 14)], $a = 2662.3$ (5) [1442.1 (3)], $b = 1433.5$ (2) [1944.8 (4)], $c = 1953.3$ (4) [2119.7 (5)] pm, $\beta = 132.75$ (1) [106.88 (2)]°, $V = 5.474$ [5.689] nm^3, $Z = 4$ [4], $D_{calc} = 1.02$ [1.10] g cm^{-3}, μ (MoK_α) = 0.19 [0.11] mm^{-1}, *F* (000) = 1856 [2032]. A total of 7143 [7351] unique reflections were recorded of which 605 [3750] were considered as unobserved [$F < 4\sigma(F)$], leaving 6538

[3601] for solution and refinement (485 [613] parameters). The final residuals were $R = 0.036$ [0.076] and $R_w = 0.036$ [0.077] with weighting scheme $w^{-1} = \sigma^2(F) + gF^2$ ($g = 0.0005$ [0.0008]). The structures were solved by direct methods. All nonhydrogen atoms were refined anisotropically. The hydrogen atoms were localized by difference electron density determination and refined using a "riding" model. Selected bond lengths and angles are given in Tables 1 and 2 and atomic coordinates in Tables 3 and 4. Additional material is available from the Cambridge Crystallographic Data Centre.

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