Structure and Conformation of Molecules R_3PCHPR_2 and $R_3SiNHPR_2$

Hubert Schmidbaur,* Annette Schier, Sybille Lauteschläger, Jürgen Riede, and Gerhard Müller

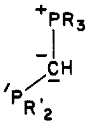
Anorganisch-chemisches Institut der Technischen Universität München, D-8046 Garching, Federal Republic of Germany

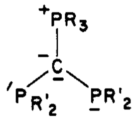
Received June 25, 1984

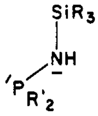
Triphenylphosphonium (diisopropylphosphino)methylide, $Ph_3PCHP(i\text{-}Pr)_2$ (1), was synthesized from $Ph_3P{=}CH_2$ and $(i\text{-}Pr)_2PCl$. Its NMR data suggest a conformation with the lone pair of electrons at the P^{III} atom in a trans orientation relative to the ylide C–H bond. The $i\text{-}Pr_2PCH$ pyramid shows one of the highest activation barriers of inversion recorded for tertiary phosphines (≫40 kcal/mol). The ^{13}C NMR spectrum of 1 displays diastereotopic methyl groups for the neat liquid even at +200 °C. Severe electronic repulsion of the carbanionic and phosphine lone pairs in the transition state are a plausible explanation for this phenomenon. The X-ray crystal structure analysis of $Ph_3SiNHPPh_2$, 2 (containing an isoelectronic skeleton), confirmed the conformational predictions for 1. 2 crystallizes in the triclinic space group $P\bar{1}$ with $a = 9.914$ (5) Å, $b = 14.418$ (8) Å, $c = 19.558$ (9) Å, $\alpha = 110.48$ (4)°, $\beta = 103.54$ (4)°, $\gamma = 99.21$ (4)°, $V = 2454.6$ Å^3, and $d_{calcd} = 1.244$ g/cm^3 for $Z = 4$ at −40 °C. Full-matrix least-squares refinement produced $R = 0.083$, $R_w = 0.084$, $w = k/\sigma^2(F_o)$, and $k = 2.6$ for 295 refined parameters and 5382 observed reflections with $F_o \geq 4.0\sigma(F_o)$. Both crystallographically independent molecules show a trans conformation of the P^{III} lone pair and the N–H bond as a consequence of the minimization of steric and electronic repulsive interactions. A comparison with the structures of related molecules, such as diphosphinoamines or phosphino ylides, shows the close parallels.

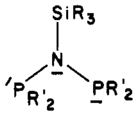
Phosphorus ylides bearing phosphino substituents, $R_3P{=}CHPR'_2$ and $R_3P{=}C(PR'_2)_2$ (A, B), show interesting conformational phenomena due to specific interactions of the lone pairs of electrons at the phosphorus atoms and at the carbanionic centers of the ylidic function.[1,2] The conformations with a perpendicular orientation of the p_z lone pair at a planar carbon and the hybrid lone pair at phosphorus are strongly favored in solution and in the crystal, as shown by NMR spectroscopy and X-ray diffraction, respectively.[1,2]

Similar conformational preferences were detected for the isoelectronic (silylamino)phosphines, $R_3SiNHPR'_2$ and $R_3SiN(PR'_2)_2$ (C, D).[3] Structures B and D render the three-coordinate phosphorus atoms nonequivalent in the NMR spectra at lower and ambient temperature, but at elevated temperature virtual equivalence is observed.[1,2]


A


B


C


D

The origin of this high-temperature equilibration process could be a release of hindered P^{III}–C bond rotation or a faster pyramidal inversion at $-PR'_2$. Although the latter was deemed unlikely,[1-3] not the least because the phenomenon was absent in the arsenic and antimony homologues,[4,5] a contribution from the inversion process could not be ruled out completely.

Unfortunately, the energy barrier for phosphorus inversion at a carbanionic center (as in ylides) has never been directly determined.[6-8] It is known, however, that aminophosphines (such as C) appear to have much higher activation energies for inversion than triorganophosphines.[7,8] The isoelectronic principle[9] would therefore suggest that molecules of type A should also be characterized by inversion rigidity.

In order to clarify this point, an ylide, A, was synthesized with NMR diagnostic isopropyl substituents R′ at the three-coordinate phosphorus atom.[10] Its high-temperature behavior should indicate directly the inversion behavior of tertiary phosphines with one carbanionic substituent. As no direct information as to the true ground-state structure of molecules A/C was available, a single-crystal X-ray diffraction study of the compound $Ph_3SiNHPPh_2$ was also initiated, and the results are included in this paper.

Conformational properties of a series of related molecules were the subject of a number of publications recently,[4,5,11-18] and a consistent picture appears to emerge from these studies as the experimental data become more and more comprehensive.

I. Conformation and Inversion Barrier of Phosphino-Substituted Ylides, $R_3P{=}CHPR'_2$. Triphenyl-

---

(1) Schmidbaur, H.; Deschler, U.; Milewski-Mahrla, B. *Chem. Ber.* **1983**, *116*, 1393.

(2) Schmidbaur, H.; Strunk, S.; Zybill, C. E. *Chem. Ber. 116*, **1983**, 3559.

(3) Schmidbaur, H.; Lauteschläger, S.; Köhler, F. H. *J. Organomet. Chem.*, in press.

(4) Schmidbaur, H.; Milewski-Mahrla, B.; Müller, G.; Krüger, C. *Organometallics* **1984**, *3*, 38.

(5) Schmidbaur, H.; Nussstein, P.; Müller, G. *Z. Naturforsch.*, in press.

(6) Horner, L.; Winkler, D. *Tetrahedron Lett.* **1964**, 161, 461. Horner, L.; Balzer, W. D.; Peterson, D. J. *Tetrahedron Lett.* **1966**, 3315.

(7) Rauk, A.; Allen, L. C.; Mislow, K. *Angew. Chem.* **1970**, *82*, 453; *Angew. Chem., Int. End. Engl.* **1970**, *9*, 400. Lehn, J.-M. *Fortschr. Chem. Forsch.* **1970**, *15*, 311.

(8) Rauk, A.; Andose, J.-D.; Frick, W. G.; Tang, R.; Mislow, K. *J. Am. Chem. Soc.* **1971**, *93*, 6507.

(9) Schmidbaur, H. *Adv. Organomet. Chem.* **1970**, *9*, 260; *Fortschr. Chem. Forsch.* **1969**, *13*, 167; *Allg. Prakt. Chem.* **1967**, *18*, 138; *J. Organomet. Chem.* **1980**, *200*, 287.

(10) We thank Professor W. Malisch, Würzburg, for drawing our attention to this method.

(11) Schmidbaur, H.; Zybill, C. E.; Krüger, C.; Krauss, H. J. *Chem. Ber.* **1983**, *116*, 1955.

(12) Rankin, D. H.; Ebsworth, E. A. V.; Zimmer-Gasser, B.; Schmidbaur, H. *Chem. Ber.* **1980**, *113*, 1637.

(13) Schmidbaur, H.; Lauteschläger, S.; Milewski-Mahrla, B. *Chem. Ber.* **1983**, *116*, 1403.

(14) Schmidbaur, H.; Schier, A.; Milewski-Mahrla, B.; Schubert, U. *Chem. Ber.* **1982**, *115*, 722.

(15) Vincent, M. A.; Schaefer III, H. F.; Schier, A.; Schmidbaur, H. *J. Am. Chem. Soc.* **1983**, *105*, 3806.

(16) Schmidbaur, H.; Schier, A.; Neugebauer, D. *Chem. Ber.* **1983**, *116*, 2173.

(17) Schmidbaur, H.; Herr, R.; Riede, J. *Chem. Ber.* **1984**, *117*, 2322.

(18) See, e.g.: Nöth H. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1984**, *39B*, 744.

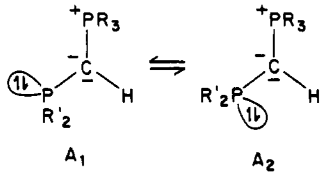
0276-7333/84/2303-1906$01.50/0

phosphonium (diisopropylphosphino)methylide (1) is available through established transylidation methods[19-22] from triphenylphosphonium methylide and chlorodiisopropylphosphine. The product first appears as a yellow

$$2(C_6H_5)_3P{=}CH_2 + (i\text{-}C_3H_7)_2PCl \rightarrow [(C_6H_5)_3PCH_3]^+Cl^- + \underset{\mathbf{1}}{(C_6H_5)_3P{=}CHP(i\text{-}C_3H_7)_2} \quad (1)$$

oil, which can be crystallized from toluene at low temperature. The $^{31}P\{^1H\}$ NMR spectrum of compound 1 in benzene at room temperature shows an AB pattern, the chemical shifts and coupling constants of which are in good agreement with those of homologues studied previously.[19,23] It is well established that $^2J(P^V\text{–}P^{III})$ in particular is very sensitive to torsional angles and may vary between very low (or even negative) values and +150 Hz as the lone pair of electrons at phosphorus P^{III} is rotated relative to the PCP plane.[24] Close agreement of $^2J(PP)$ in the $R_3P{=}CHPR'_2$ series is therefore good evidence for a common rotational ground state (A_1 or A_2) of these molecules. From species of type B the NMR data of the two opposite conformations (A_1, A_2) can be extracted simultaneously, but assignments to the cis and trans orientation of the P^{III} lone pair are not unambiguous.[1,2]

From a consideration of steric effects, preference is given intuitively to conformation A_1. This suggestion was indeed shown to be correct by the results of the X-ray analysis described below for a member of the isoelectronic series $R_3SiNHPR'_2$. It is to be noted that both an inversion at P^{III} or a C–P^{III} bond rotation would lead to interconversion of A_1 and A_2.



The ^1H NMR spectrum of 1 is rather complex, as expected, and even ^{31}P decoupling does not allow complete and unambiguous signal assignment. The $^{13}C\{^1H\}$ NMR spectrum, however, can be easily assigned to the postulated structural units of the molecule (see Experimental Section). Most important, the spectrum is proof for nonequivalent methyl carbon atoms in each isopropyl group. Those diastereotopic methyl groups indicate directly the pyramidal rigidity at the P^{III} center. Moreover, configurational stability of the tertiary phosphine is retained over the full temperature range available (−80 to +200 °C). The measurements at the high-temperature limit were carried out in the absence of a solvent with the neat liquid, which is thermally stable to 200 °C. No sign of line broadening was registered even above this limit.[25]

Estimations using standard energy correlations lead to the conclusion that an activation barrier of greater than 40 kcal/mol is required for pyramidal inversion at a phosphine attached to an ylidic carbanion as in 1 (A), if the usual δ and J values are applied. Thus phosphino ylides have *one of the highest inversion barriers of teriary phosphines* reported in the literature.[6,8]

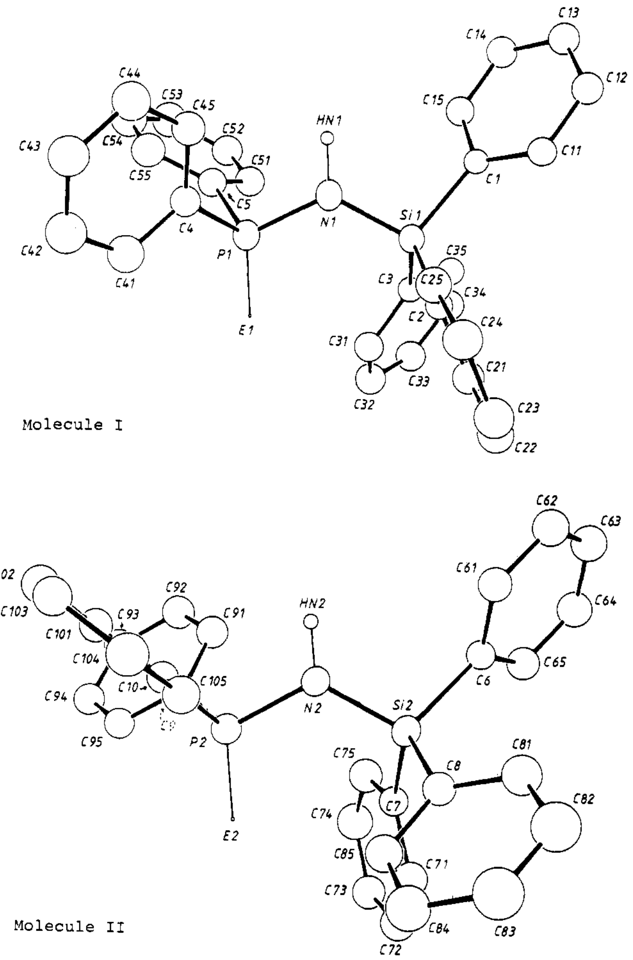
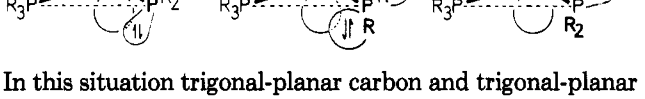


Figure 1. Perspective view of both independent molecules of 2 with atomic numbering scheme (ORTEP) (anisotropic thermal ellipsoids (50%) for atoms P, N, and Si; phenyl carbon atoms with root-mean-square deviation of the isotropic thermal parameter as radius; hydrogen atoms have been omitted for clarity with the exception of those at nitrogen, which are shown with an arbitrary radius).

As with the corresponding *alkoxy-* or *aminophosphines*,[7,8] the reason for extremely high inversion barriers is to be attributed to unfavorable lone pair interactions in the transition state of inversion:



In this situation trigonal-planar carbon and trigonal-planar phosphorus interact most strongly through p_z lone pairs at both centers.

This model confirms the bonding concept of ylides.[15,26,27] It also is definite proof that conformational interconversions in A or B are to be attributed solely to rotational phenomena, with no contributions from phosphorus inversion.[1,4,5]

II. The Conformation of (Silylamino)phosphines, $R_3SiNHPR'_2$.

An X-ray diffraction study was desirable

---

[19] Issleib, K.; Lindner, R. *Liebigs Ann. Chem.* **1966**, *699*, 40.

[20] Schmidbaur, H. *Acc. Chem. Res.* **1975**, *8*, 62; *Adv. Organomet. Chem.* **1976**, *14*, 205.

[21] Seyferth, D.; Singh, G.; Suzuki, R. *Pure Appl. Chem.* **1968**, *13*, 159.

[22] Bestmann, H. J. *Chem. Ber.* **1962**, *95*, 58.

[23] Harris, R. K.; Woplin, J. R.; Issleib, K.; Lindner, R. *J. Magn. Reson.* **1972**, *7*, 291.

[24] See references in ref 1.

[25] Jackman, L. M.; Cotton, F. A., "Dynamic NMR Spectroscopy"; Academic Press: New York, 1975.

[26] Wittig, G. *Angew. Chem.* **1956**, *68*, 505; **1980**, *92*, 671; *Acc. Chem. Res.* **1974**, *7*, 6.

[27] Schmidbaur, H. *Angew. Chem.* **1983**, *95*, 980; *Angew. Chem., Int. Ed. Chem.* **1983**, *22*, 907.

Table I. Fractional Atomic Coordinates for 2 with Esd's in Parentheses

atom	*x/a*	*y/b*	*z/c*
P1	0.2818 (2)	0.1831 (1)	0.0414 (1)
P2	0.2700 (1)	0.1635 (1)	0.5234 (1)
Si1	0.0905 (1)	0.3262 (1)	0.0266 (1)
Si2	0.0890 (2)	0.3136 (1)	0.5233 (1)
N1	0.1230 (4)	0.2156 (3)	0.0358 (2)
N2	0.1119 (4)	0.1962 (3)	0.5223 (2)
C1	−0.1099 (5)	0.2976 (4)	−0.0003 (3)
C11	−0.1825 (5)	0.3598 (4)	0.0415 (3)
C12	−0.3332 (6)	0.3316 (4)	0.0209 (3)
C13	−0.4125 (6)	0.2412 (4)	−0.0412 (3)
C14	−0.3439 (6)	0.1794 (4)	−0.0848 (3)
C15	−0.1940 (5)	0.2078 (4)	−0.0637 (3)
C2	0.1790 (5)	0.4435 (4)	0.1177 (3)
C21	0.2522 (6)	0.5355 (4)	0.1191 (3)
C22	0.3124 (6)	0.6239 (4)	0.1873 (3)
C23	0.2993 (6)	0.6207 (4)	0.2557 (3)
C24	0.2279 (6)	0.5317 (4)	0.2560 (3)
C25	0.1703 (6)	0.4428 (4)	0.1886 (3)
C3	0.1545 (5)	0.3487 (4)	−0.0513 (3)
C31	0.3022 (6)	0.3727 (4)	−0.0425 (3)
C32	0.3501 (6)	0.3906 (4)	−0.0999 (3)
C33	0.2503 (6)	0.3864 (4)	−0.1645 (3)
C34	0.1060 (6)	0.3639 (4)	−0.1741 (3)
C35	0.0584 (6)	0.3459 (4)	−0.1167 (3)
C4	0.3103 (6)	0.1390 (4)	0.1199 (3)
C41	0.4547 (6)	0.1571 (4)	0.1619 (3)
C42	0.4881 (6)	0.1251 (5)	0.2218 (4)
C43	0.3806 (6)	0.0762 (5)	0.2393 (4)
C44	0.2377 (6)	0.0549 (4)	0.1970 (3)
C45	0.2041 (6)	0.0872 (4)	0.1372 (3)
C5	0.2291 (6)	0.0591 (4)	−0.0416 (3)
C51	0.1673 (6)	0.0558 (4)	−0.1153 (3)
C52	0.1320 (6)	−0.0341 (5)	−0.1800 (4)
C53	0.1569 (6)	−0.1230 (5)	−0.1743 (4)
C54	0.2190 (6)	−0.1216 (5)	−0.1027 (4)
C55	0.2567 (6)	−0.0308 (5)	−0.0364 (4)
C6	−0.1097 (5)	0.2994 (4)	0.4961 (3)
C61	−0.1913 (6)	0.2684 (4)	0.5382 (3)
C62	−0.3386 (6)	0.2574 (4)	0.5184 (3)
C63	−0.4080 (6)	0.2774 (4)	0.4569 (3)
C64	−0.3310 (6)	0.3085 (4)	0.4157 (3)
C65	−0.1821 (6)	0.3202 (4)	0.4351 (3)
C7	0.1688 (5)	0.3379 (4)	0.4519 (3)
C71	0.2712 (6)	0.4284 (4)	0.4697 (3)
C72	0.3335 (6)	0.4426 (4)	0.4164 (3)
C73	0.2970 (6)	0.3651 (4)	0.3438 (3)
C74	0.1934 (6)	0.2757 (5)	0.3235 (4)
C75	0.1295 (6)	0.2616 (4)	0.3771 (3)
C8	0.1802 (5)	0.4220 (4)	0.6203 (3)
C81	0.1050 (6)	0.4851 (4)	0.6575 (3)
C82	0.1760 (6)	0.5670 (5)	0.7311 (4)
C83	0.3174 (6)	0.5832 (5)	0.7648 (4)
C84	0.3986 (6)	0.5232 (5)	0.7296 (4)
C85	0.3290 (6)	0.4430 (4)	0.6573 (3)
C9	0.2268 (5)	0.0460 (4)	0.4363 (3)
C91	0.0880 (6)	−0.0078 (4)	0.3871 (3)
C92	0.0662 (6)	−0.0967 (4)	0.3217 (3)
C93	0.1816 (6)	−0.1312 (4)	0.3050 (3)
C94	0.3198 (6)	−0.0785 (4)	0.3538 (3)
C95	0.3414 (6)	0.0098 (4)	0.4186 (3)
C10	0.2907 (5)	0.1099 (4)	0.5969 (3)
C101	0.2820 (5)	0.0082 (4)	0.5834 (3)
C102	0.3046 (6)	−0.0247 (4)	0.6432 (3)
C103	0.3357 (6)	0.0453 (4)	0.7179 (3)
C104	0.3446 (6)	0.1483 (4)	0.7332 (3)
C105	0.3234 (6)	0.1808 (4)	0.6733 (3)

for the determination of the rotational ground-state structure of A or C. The pentaphenyl homologue of the $R_3SiNHPR_2$ series was obtained as a byproduct of attempted preparations for bis(phosphino)silylamines, $R_3SiN(PR'_2)_2$.[3] The compound 2 had been prepared previously from diphenylphosphine and triphenylsilyl azide.[28]

Table II. Selected Interatomic Distances and Angles (deg) and Some Torsion Angles for 2

molecule I		molecule II	
	Bond Distances		
P1-N1	1.703 (4)	P2-N2	1.705 (4)
Si1-N1	1.737 (4)	Si2-N2	1.737 (4)
P1-C4	1.840 (5)	P2-C9	1.835 (5)
P1-C5	1.838 (5)	P2-C10	1.842 (5)
Si1-C1	1.868 (5)	Si2-C6	1.873 (5)
Si1-C2	1.867 (5)	Si2-C7	1.864 (5)
Si1-C3	1.887 (5)	Si2-C8	1.878 (5)
	Bond Angles		
P1-N1-Si1	125.5 (3)	P2-N2-Si2	123.0 (2)
N1-P1-C4	104.7 (2)	N2-P2-C9	105.6 (2)
N1-P1-C5	102.3 (2)	N2-P2-C10	101.8 (2)
C4-P1-C5	99.9 (2)	C9-P2-C10	100.3 (2)
N1-Si1-C1	102.6 (2)	N2-Si2-C6	106.3 (2)
N1-Si1-C2	112.5 (2)	N2-Si2-C7	106.7 (2)
N1-Si1-C3	111.9 (2)	N2-Si2-C8	112.6 (2)
C1-Si1-C2	111.5 (2)	C6-Si2-C7	112.4 (2)
C1-Si1-C3	110.6 (2)	C6-Si2-C8	109.5 (2)
C2-Si1-C3	107.8 (2)	C7-Si2-C8	109.4 (2)
	Torsion Angles		
P1-N1-Si1-C1	166.5	P2-N2-Si2-C6	165.8
P1-N1-Si1-C2	−73.6	P2-N2-Si2-C7	45.6
P1-N1-Si1-C3	48.0	P2-N2-Si2-C8	−74.3
Si1-N1-P1-C4	135.2	Si2-N2-P2-C9	−121.7
Si1-N1-P1-C5	−121.0	Si2-N2-P2-C10	133.9

The material forms colorless, moisture-sensitive crystals. Isolation from multicomponent reaction mixtures is difficult, however, and yields are generally disappointing.

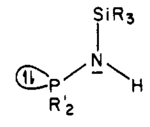
$$Ph_3SiCl/Ph_2PCl/NH_3 \text{ or } (Ph_2P)_2NH/Ph_3SiCl \rightarrow Ph_3SiNHPPh_2 \quad (2)$$

2

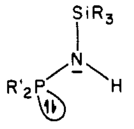
The results of the structure determination are summarized in Tables I and II and in Figure 1. The unit cell contains two crystallographically independent individual molecules (I and II) with very similar structures. The most noteworthy differences arise from the relative orientations of the phenyl rings as regards the rotation about their P–C and Si–C bonds, respectively. An inspection of Figure 1 shows that both molecules are approximately mirror images, but not identical. The situation amounts to a coexistence of both enantiomers in the asymmetric unit.

The orientation of the lone pair of electrons at phosphorus (designated E) was calculated as the vector pointing to the missing tetrahedral corner, and the hydrogen atom attached to nitrogen could be located for both molecules in difference Fourier syntheses with satisfactory precision, but was not refined. In both molecules these hydrogen atoms lie well in the plane of the PNSi skeletons.

Clearly, the molecules adopt the expected cis configuration of the lone pair of electrons at phosphorus relative to the Si–N bond. The conformations thus correspond to formula C_1, the analogue of A_1 of the isoelectronic ylide.



C_1



C_2

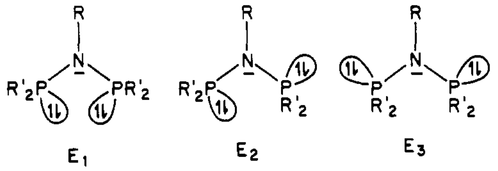
The calculated lone-pair vectors (P→E) have torsional angles SiNPE of 7.5 and 5.5° for molecules I and II, respectively. To use another description, the lone pairs E are in a trans position relative to the hydrogen atoms at nitrogen in I or II, and hence the torsional angles EPNH amount to 173.6 and −177.4°.

---

(28) Paciorek, K. L.; Kratzer, R. H. *J. Org. Chem.* **1966**, *31*, 2426.

The lone pair at P^{III} approximately bisects the angles C2–Si1–C3 and C7–Si2–C8, i.e., the angle between the two phenyl rings. The hydrogen on the bridging nitrogen, on the other hand, is staggered with respect to the P–phenyl bonds. An HNSiC eclipse becomes evident, however, from the small torsional angles C1–Si1–N1–HN1 = 1.2° and C6–Si2–N2–HN2 = −11°. Apparently, the conformation is determined by the steric interaction of the P^{III} lone pair with the other two phenyl rings at silicon.

In this connection it is interesting to note that in the crystals of bis(diphenylphosphino)amines conformation E_1 is favored over E_2 if the substituent R is sterically nondemanding,[18,29,30] but in solution at very low temperatures conformation E_2 prevails according to NMR data (R = H, R′ = Ph).[30] Only with R = *i*-Pr and R′ = Ph conformation E_2 is also valid in the solid state.[30] Compound 2 resembles E_2 and, therefore, the repulsion of P^{III} lone pairs and the phenyl groups at silicon again appear to be the dominating force, with a trigonal-planar geometry at nitrogen and a perpendicular orientation of its p lone pair with the sp^n lone pair at phosphorus as the basic features of the skeleton.



Bond distances and angles of the two molecules of 2 have no unusual features and are well within standard dimensions of related compounds (Table II).

Experimental Section

The experiments were carried out under dry, purified nitrogen. Solvents and glassware were dried and saturated or filled with nitrogen, respectively.

Triphenylphosphonium (Diisopropylphosphino)methylide (1). A 10.0-g (36.2-mmol) sample of triphenylphosphonium methylide[32] was dissolved in 100 mL of toluene and heated to 60 °C, before 2.54 g (16.6 mmol) of chlorodiisopropylphosphine, dissolved in 20 mL of toluene, was added with stirring. A precipitate was formed, and the color of the solution changed from orange to yellow. The reaction mixture was filtered and the solvent removed from the filtrate under vacuum, leaving the product as a yellow oil, which crystallized from toluene at −40 °C: yield 4.9 g (76 %); ^1H NMR (C_6D_6) δ 0.32–2.12 (m, 15 H), 6.80–8.10 (m, 15 H); ^{31}P NMR (C_6D_6) δ −3.5 (d, P^{III}), 22.0 (d, P^V, $^2J(PP)$ = 131.2 Hz); the spectrum is unchanged at 75 °C; ^{13}C NMR (C_6D_6, 35 °C) δ 2.31 (dd, P=CHP, $^1J(PC)$ = 121.1 and 21.5 Hz), 26.8 (dd, PCHC, $^1J(PC)$ = 10.0, $^3J(PC)$ = 8.0 Hz), 21.3 (d, CH_3, $^2J(PC)$ = 20.4 Hz), 19.2 (d, CH_3, $^2J(PC)$ = 6.8 Hz), 128.3 (d, C3, $^3J(PC)$ = 11 Hz), 133.7 (dd, C2, $^2J(PC)$ = 9, $^4J(PC)$ = 2 Hz), 130.0 (d, C4 $^4J(PC)$ = 3 Hz), 134.0 (dd, C1, $^1J(PC)$ = 87, $^3J(PC)$ = 3 Hz). Anal. Calcd for $C_{25}H_{30}P_2$ (392.45): C, 76.51; H, 7.70. Found: C, 75.97; H, 7.62. Apart from minor changes in the chemical shifts, the spectrum of the neat liquid was identical at +30 and +200 °C (a sealed and centered capillary filled with Me_2SO-d_6 was used as a lock reference) (Figure 2).

[(Triphenylsilyl)amino]diphenylphosphine (2). The compound was obtained as a byproduct of reactions indicated in eq 2. It forms colorless crystals with properties corresponding to those of a material prepared previously.[28]

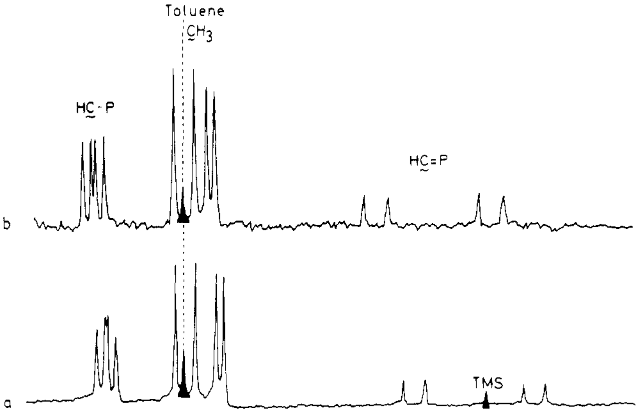


Figure 2. ^{13}C NMR spectrum of compound 1 (aliphatic region). (a) Spectrum of a benzene solution at 30 °C containing a trace of toluene and tetramethylsilane, ^1H decoupled. (b) Spectrum of the neat liquid at 200 °C containing a trace of toluene, ^1H decoupled.

X-ray Structure Determination of 2. Crystal data: $C_{30}H_{26}NPSi$, M_r = 459.61, triclinic, space group $P\bar{1}$, a = 9.914 (5) Å, b = 14.418 (8) Å, c = 19.558 (9) Å, α = 110.48 (4)°, β = 103.54 (4)°, γ = 99.21 (4)°, V = 2454.6 Å^3, d_{calcd} = 1.244 g/cm^3 for Z = 4; $F(000)$ = 968, T = −40 °C. The exact cell constants were determined by a least-squares fit of the parameters of the orientation matrix to the setting angles of 15 high-order reflections from various parts of reciprocal space. Reduced cell calculations did not reveal any symmetry higher than triclinic. A total of 6795 unique reflections were collected on an automated four-circle diffractometer (Syntex $P2_1$) using graphite-monochromated Mo Kα radiation (λ = 0.71069 Å; ω scans; $1 \leq \theta \leq 24°$). The stability of the crystal and diffractometer system was checked by monitoring one standard reflection (004) that was repeated every 50 reflections. No systematic variation in its intensity was observed. Due to the highly irregular crystal shape an empirical absorption correction was undertaken that was based on the intensity variation of scans around the diffraction vectors of nine selected reflections (μ(Mo Kα) = 1.73 cm^{-1}, Syntex XTL). The structure was solved by direct methods (MULTAN 80) and completed by Fourier methods. All hydrogen atoms could be located in difference maps. Refinement of 295 parameters on 5383 "observed" ($F_o \geq 4.0\sigma(F_o)$) reflections converged at R = 0.083, R_w = 0.084 ($w = k/\sigma^2(F_o)$, and k = 2.6 in the last cycle: P, N, and Si atoms anisotropic; phenyl C atoms isotropic; H atoms fixed with U = 0.05 Å^2; maximum shift/error ratio in last cycle <0.01, SHELX 76. Further details of the data collection, data reduction, and refinement procedures as well as a list of the used programs and the sources of the scattering factors may be found elsewhere.[31] A final difference Fourier synthesis was qualitatively featureless, $\Delta\rho_{max/min}$ = +0.94 and −0.59 e/Å^3, with the maxima resulting clearly from the isotropic treatment of the phenyl C atoms. Table I contains the final atomic coordinates, and Table II summarizes important bond lengths and angles.

Acknowledgment. This work was supported by Deutsche Forschungsgemeinschaft, Bonn-Bad Godesberg, and by Fonds der Chemischen Industrie, Frankfurt. Hoechst AG, Frankfurt, is thanked for a generous gift of chemicals.

Registry No. 1, 92220-64-9; 2, 7351-38-4.

Supplementary Material Available: Tables of thermal parameters and hydrogen atom parameters and lists of observed and calculated structure factor amplitudes for 2 (32 pages). Ordering information is given on any current masthead page.

---

(29) Müller, G. unpublished results (1983).

(30) Keat, R.; Manojlović-Muir, L.; Muir, K. W.; Rycroft, D. S. *J. Chem. Soc., Dalton Trans.* **1981**, 2192 and references therein.

(31) Wiberg, N.; Wagner G.; Müller, G.; Riede, J. *J. Organomet. Chem.* **1984**, *271*, 381.

(32) Schmidbaur, H.; Stühler, H.; Vornberger, W. *Chem. Ber.* **1972**, *105*, 1084.