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ISOMERISM AND CONFORMATION OF (*N*-SILYL)BIS(DIPHENYLPHOSPHINO)AMINES AND BIS(*N*-SILYL)-DIPHENYLPHOSPHINOAMINES *

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Summary

Lithium bis(diphenylphosphino)amide (**2**) reacts with chlorotriorgano- and dichlorodiorganosilanes to form either *N*-silylbis(diphenylphosphino)amides (**3**) or the isomeric *P*-diphenylphosphinodiphenylphosphine(silylimides) (**4**), or an equilibrium mixture of both. The nature of the product depends strongly on the nature of the substituents attached to silicon. ^{29}Si and ^{31}P NMR spectroscopy were used to differentiate between the two structures.

In *N*,*N*-bis(trimethylsilyl)aminodiphenylphosphine the two silyl groups were found by NMR spectroscopy to be non-equivalent at low temperature in solution, and this is attributed to hindered rotation about the P–N bond, with an in-plane (Si_2NP) orientation of the lone pair of electrons at phosphorus as the ground state. The reaction of **2** with $(CH_3)_2PCl$ does not yield triphosphinoamine species; instead, a *P*-phosphinophosphinimine (**5**) is obtained, which is closely related to the silyl analogues of formula **4**.

Introduction

Trisilylamines I have for many years attracted considerable attention [1]. The bonding and reactivity of the planar NSi_3 skeleton are of continued interest to the theoretical and synthetic chemist. In contrast, the corresponding triphosphinoamines IIa are still virtually unknown [2]. Attempts at synthesis have almost invariably met with failure, the reported existence of $(F_2P)_3N$ and $[(CH_3)_2P]_3N$ being exceptional [3]. It appears that the P–P bonded isomers IIb are clearly favoured energetically, and definitely represent the energy minimum for the homoleptic system.

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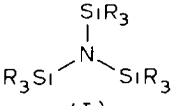
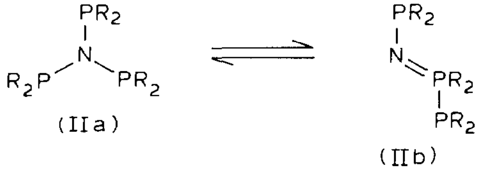
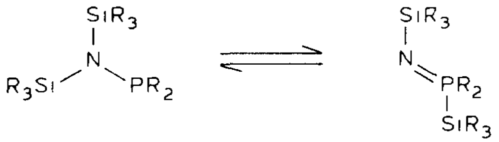
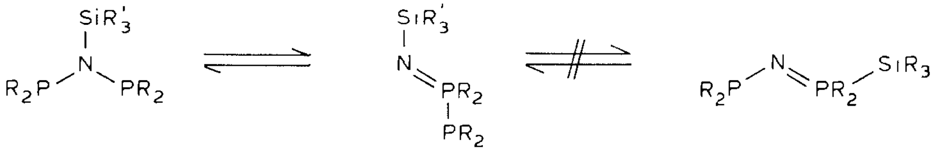
Among mixed systems the bis(*N*-silyl)phosphinoamines IIIa have also been extensively studied, but no indication of any isomerism to species of type IIIb has been reported [4–12]. P–Si bonded species IIIb seem to be energy-rich states compared to IIIa species in this family.


(I)


(IIa) (IIb)


(IIIa) (IIIb)

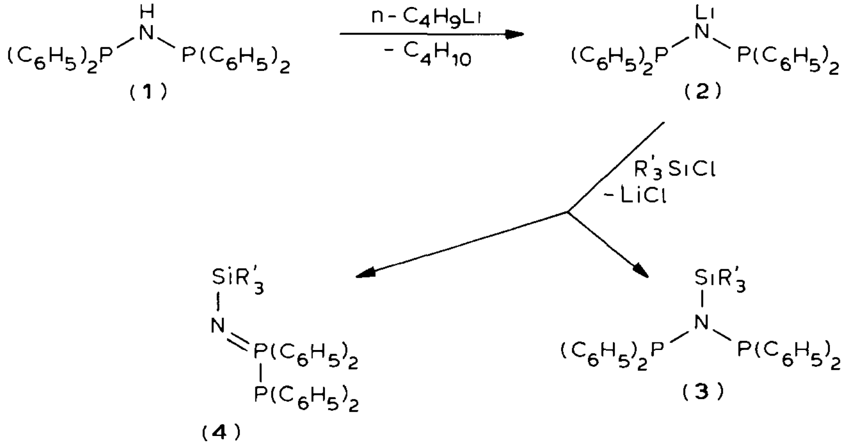
Very little is known about the remaining species IV, having an $SiNP_2$ skeleton. For two well characterized materials, $H_3SiN(PF_2)_2$ [13] and $(CH_3)_3SiN[P(C_6H_5)_2]_2$ [14], the trigonal unit of type IVa was confirmed, whereas neither of the other two possible isomers IVb, IVc could be detected. This finding is surprising, as both the P=N and the P–P moieties should favour the alternative IVb, which is closely related to IIIb.


(IVa) (IVb) (IVc)

A study was therefore initiated, in which, primarily through the choice of substituents R′ at silicon, appropriate variation of steric and/or electronic effects should induce a shift of the above equilibrium towards IVb/IVc. Where species of the type IVa (and IIIa) were encountered, investigation of their conformational preference was also necessary, since previous work with the system III had repeatedly shown that rotation about the P–N single bond and inversion barriers at P^{III} were significant for a reliable description of the pertinent molecular structures and dynamics [7–11]. Results of systematic studies of isoelectronic ylide systems are in full agreement with these predictions [15–18]. Metal bis(diphenylphosphino)amides [19] and bis(phosphino)olefins show similar relative orientations of the $P(C_6H_5)_2$ groups [20].

Preparation of *N*-silylbis(diphenylphosphino)amines

The synthetic approach adopted to give the title compounds of type IV is straightforward, and similar to that used for trisilylamines I. Lithiated bis(diphenylphosphino)amine (**2**) [14] was treated with an equimolar quantity of a chlorosilane in tetrahydrofuran at room temperature followed by heating to a temperature range from 40 to 65 °C for several hours. The yields were generally around 60–80%.



(a : $R'_3 = Me_3$, b : $R'_3 = Et_3$; c · $R'_3 = MePh_2$; d . $R'_3 = i\text{-}Pr_3$;
e $R'_3 = i\text{-}Pr_2Cl$, f . $R'_3 = Me_2Cl$, g · $R'_3 = Ph_3$, g . $R'_3 = Me_2Ph$)

Two types of products (**3,4**) were obtained, depending on the nature of R in the R_3Si substituent, as clearly shown by the spectral data of the products (below). The compounds are colourless solids with melting points in the range of 100–150 °C, and sensitive to moisture.

In three of the eight examples investigated both isomers could be detected in solution by NMR spectroscopy, their ratio either depending on the reaction conditions (**3/4e,f**), or reflecting establishment of equilibrium in solution (**3/4d**). At present no clear decision can be made about the relative stabilities of the isomers in the solid and in solution, respectively, as both may well differ in the two states.

NMR, IR and mass spectra of *N*-silylbis(diphenylphosphino)amines and their isomers

Of the NMR data the ^{31}P and ^{29}Si spectra provide most direct structural evidence. ^{31}P singlet signals are observed (^1H-decoupled) for isomers **3**, but well defined AB-systems for isomers **4**. The latter are characterized by a large P–P coupling (222 to 232 Hz), and one chemical shift is in the range for three-coordinate P^{III} while the other falls into the range for tetra-coordinate P^V.

The singlets of isomers **3** are also split into AB systems at low temperature, with coalescence points at ca. −20 °C. The resulting low-temperature patterns have small P–P couplings (ca. 10 Hz) and the two chemical shifts are roughly symmetrically displaced from the high-temperature singlets. This temperature dependence is due to a restricted rotation around the P–N single bonds, with the unsymmetrical (C_s) conformation IVa′ as the ground state, as noted previously [7–11,15–20]. The activation energies E_n, are 11.4 ± 0.5 kcal/mol in all cases, from coalescence temperature measurements.

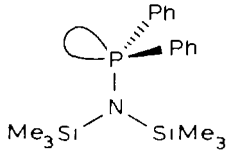
The ^{31}P NMR spectra of isomers **4** are not temperature-dependent in this temperature range. The ^{29}Si signals for isomers **3** are triplets at ambient temperatures with small $^{31}P-^{29}Si$ coupling constants, but for isomers **4** doublets appear, with $J(^{31}P-^{29}Si)$ around 20 Hz. These characteristics rule out the presence of any P–Si bonded isomers IVc, which would require much larger J-values. The coupling constants are in good agreement, however, with those reported for other silylphosphinimines (Si–N=P) [21–23] and silylaminophosphines (Si–N–P) [24,25]. The temperature dependence was not investigated. Formulae IVa and IVb clearly apply to the two isomers observed in the present study.

Formulae IVb requires a strong, relative broad absorption band due to the P=N stretching vibration, which is expected to appear in the range of 1270–1300 cm^{-1} [26–30]. In fact, compounds **4h**–**4f** show intense IR bands at 1290, 1310 and 1265 cm^{-1}, whereas the remaining species **3a**–**3e** have only weaker and sharp absorptions around 1250 cm^{-1}, assigned to $\delta(CH_3Si)$ and other vibrations [26].

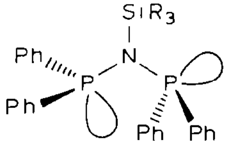
The mass spectra do not discriminate between formulae **3** or **4**. Molecular ions are observed in all cases, with fragmentation patterns depending markedly on the nature of the substituents. For **4f** the presence of the $^{35/37}Cl$ isotope pattern confirms the presence of a covalent SiCl bond.

The ^1H NMR spectra of bis(trimethylsilyl)aminodiphenylphosphine

The title compound is a known species, easily prepared from alkalimetal bis(trimethylsilyl)amides and diphenylchlorophosphine [4,14]. Its tetrahydrofuran solutions were studied by variable temperature ^1H NMR spectroscopy, and splitting of the CH_3Si singlet into a 1/1 doublet was detected below −65 °C (coalescence temperature). An activation energy E_A of 10.2 kcal/mol was calculated, for a process best described as a hindered rotation around the P–N single bond.



(IIIa′)

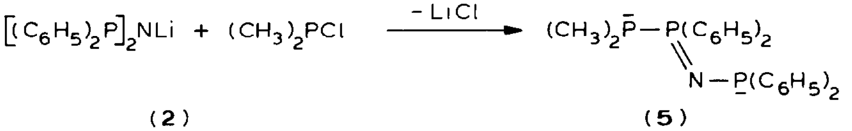


(IVa′)

A ground state with the lone pair of electrons at phosphorus in the heavy atom plane $PNSi_2$ renders the Si atoms non-equivalent. It has been pointed out previously [15–20] that inversion at phosphorus would also account for the equilibration of the silyl groups at ambient temperature. It is known, however, that phosphine inversion barriers are generally much greater than 10 kcal/mol, and so this explanation is considered unlikely.

Attempted preparation of tris(diorganophosphino)amines

It has been shown previously that the usual synthetic approaches to $[(C_6H_5)_2P]_3N$ give the isomeric $(C_6H_5)_2P-P(C_6H_5)_2=NP(C_6H_5)_2$ [4]. We have confirmed these results in our own experiments. Several modifications of the reaction conditions did not lead to the desired product with a N-centered P_3-triangle. It should be added that replacement of one $P(C_6H_5)_2$ group by $P(CH_3)_2$ also does not result in formation of a P_3N structure. A P–P bonded phosphineimine is again obtained.



The ^{31}P NMR spectra of the product resemble those of the parent hexaphenylated species. The spectra of simple reference compounds leave no doubt that the imine structure is again present [4,26–30].

Compounds of the composition $(R_2P)_2NR'$ with R' = alkyl or aryl were found previously to exist in two isomeric forms, $R_2PN(R')PR_2$ and $R_2PP(R_2)$=NR′, in close analogy to our findings above. A marked substituent effect of R′ is the origin of the isomerism observed [31,32].

Experimental

All experiments were carried out under dry purified nitrogen. Glassware was dried and filled with N_2, and solvents were dried and saturated with N_2.

Spectrometers. Jeol C60 HL, Jeol FX 60, Bruker XL 90, Bruker CXP 200 for ^1H, ^{13}C, ^{31}P and ^{29}Si, respectively; Atlas 311A in the EI and FD mode; Perkin–Elmer 577.

*Preparation of compounds, **3a**–**3c** and **4b**–**4f***

General procedure. A suspension of bis(diphenylphosphino)amine (**1**) in benzene is treated with one mole-equivalent of n-butyllithium in hexane at 0 to 20 °C for 30 min. Lithium bis(diphenylphosphino)amide (**2**) separates as a light yellow solid, which is filtered off, washed with hexane and dissolved in tetrahydrofuran to give a yellow solution. One molar equivalent of the silane is added with stirring at room temperature, and the reactions are completed by heating at 40–65 °C for several hours (see below for details). After removal of the solvents the products are extracted from the residue with benzene or toluene, and crystallized. Yields are generally between 50 and 80%.

N-Trimethylsilylbis(diphenylphosphino)amide (**3a**) [14,4], white solid, yield 80%, m.p. 104 °C. Analysis: Found: C, 70.36; H, 6.40. $C_{27}H_{29}NP_2Si$ (457.6) calcd.: C, 70.87; H, 6.39%. Molecular mass 457, M^+ (MS).

N-Triethylsilylbis(diphenylphosphino)amide (**3b**), white solid, m.p. 105 °C. Analysis: Found: C, 70.96; H, 6.90; N, 2.72; P, 11.99, Si, 5.8. $C_{30}H_{35}NP_2Si$ (499.65) calcd.: C, 72.11; H, 7.06; N, 2.80; P, 12.39; Si, 5.62%. Molecular mass 499, M^+ (MS).

N-Diphenylmethylsilylbis(diphenylphosphino)amide (**3c**), white solid, m.p. 155 °C. Analysis: Found: C, 75.83; H, 5.44; N, 2.12; P, 10.71; Si, 5.0. $C_{37}H_{33}NP_2Si$ (581.71) calcd.: C, 76.39; H, 5.71; N, 2.40; P, 10.65; Si, 4.82%. Molecular mass 581, M^+ (MS).

N-(Triisopropylsilyl)bis(diphenylphosphino)amide (**3d**) *and its isomer* **4d**. A mixture of the two isomers is obtained from reactions carried out either at 20 °C for 15 h or at 40 °C for 1 h. The products could not be crystallized and analyzed.

Identification was by spectroscopy. $C_{33}H_{41}NP_2Si$ (541.72) molecular mass 541, M^+ (MS). $m/e = 498$ ($M - C_3H_7$), 499 ($M - C_3H_6$), 357 ($M - PC_{12}H_{10}$).

N-(Chlorodiisopropylsilyl)bis(diphenylphosphino)amide (**3e**) *and its isomer* **4e**. The product is predominantly **3e** from reactions carried out at 40 °C for 1 h, but **4e** from reactions at 20 °C for 15 h. The materials could not be crystallized and analyzed. Identification was by ^{31}P NMR spectroscopy (see below).

N-(Chlorodimethylsilyl)bis(diphenylphosphino)amide (**4f**) *and its isomer* **3f**. **4f** is formed after 15 h at 20 °C, while **3f** is obtained after 30 min at 40 °C followed by 10 min at 80 °C. Long reaction times at 20 °C ($\geq$ 20 h) give a mixture of **3f** and **4f**. The products could not be crystallized and analyzed. $C_{26}H_{26}ClNP_2Si$ (477.91) molecular mass 477/479, M^+ (MS) for ^{35}Cl and ^{37}Cl isotopes (3/1).

Diphenylphosphino(diphenyl)[triphenylsilylimino]phosphorane (**4g**), white solid, m.p. 148 °C. Analysis: Found: C, 76.57; H, 5.76; N, 1.73; P, 10.06; Si, 4.5. $C_{42}H_{35}NP_2Si$ (643.78) calcd.: C, 78.36; H, 5.48; N, 2.77; P, 9.62; Si, 4.36%. Molecular mass 643, M^+ (MS); 458 ($M - PC_{12}H_{10}$), 259 ($SiC_{18}H_{15}$).

Diphenylphosphino(diphenyl)[dimethylphenylsilylimino]phosphorane (**4h**), white solid, m.p. 95 °C. Analysis: Found: C, 70.03; H, 5.96; N, 2.45; P, 11.64; Si, 5.9. $C_{32}H_{31}NP_2Si$ (519.64) calcd.: C, 73.96; H, 6.01; N, 2.70; P, 11.92; Si, 5.40%. Molecular mass 519, M^+ (MS); 442 ($M - C_6H_5$); 334 ($M - PC_{12}H_{10}$).

Dimethylphosphino(diphenyl)[(diphenylphosphino)imino]phosphorane (**5**). The compound is obtained as described for **3** or **4** from **2** and $(CH_3)_2PCl$. Its ^{31}P NMR spectrum (δ, ppm) can be consistently interpreted by the following set of parameters:

$Me_2{}^{B}P{-}Ph_2{}^{A}P{=}N{-}{}^{X}PPh_2$: δ_A 22.1, dd, $^1J_{AB}$ 230, $^2J_{AX}$ 113 Hz; δ_B −19.0, dd, $^3J_{BX}$ 6 Hz; δ_X 40.7, dd.

$Ph_2{}^{B}P{-}Ph_2{}^{A}P{=}N{-}{}^{X}PPh_2$: (for comparison [4]): δ_A 20.15, dd, $^1J_{AB}$ 249, $^2J_{AX}$ 93 Hz. δ_B −10.6, d, $^3J_{BX}$ small. δ_X 40.15, d.

^{1}H NMR spectra: The ^{1}H spectra (δ, ppm) of the compounds **3** and **4** show an aryl multiplet between 6.5 and 7.6 ppm, in correct intensity ratio with the alkyl signals. The chemical shifts of these alkyl resonances are as follows: δ −0.2, s, CH_3, **3a**; 0.5, A_3B_2, C_2H_5, **3b**; 0.6, A_6B, C_3H_7, **3d** and **3e**; −0.1, s, CH_3, **3c** and **4h**; 0, s, CH_3, **4f** (C_6D_6 was used as a solvent, δ relative TMS, 30 °C).

^{29}Si NMR spectra: Proton-decoupled ^{29}Si spectra were obtained from C_6D_6 solution containing $Cr(acac)_3$ as a relaxation promotor at 30 °C. δ was measured relative hexamethyldisiloxane and converted to TMS.

3a: δ 9.19, t, ^2J(PSi) 7.6 Hz
3b: δ 14.62, t, ^2J(PSi) 4.4 Hz
3c: δ −7.62, t ^2J(PSi) 3.5 Hz
3f: δ 14.59, t, ^2J(PSi) 5.5 Hz
4f: δ −13.42, d, ^2J(PSi) 23.2 Hz
} Int. ratio 1/2.8.
4g: δ −20.58, d, ^2J(PSi) 23.5 Hz
4h: δ −25.87, d, ^2J(PSi) 19.1 Hz

Reference compounds [21]:
$Me_3P{=}N{-}SiMe_3$ δ −13.75, ^2J(PSi) 18.6 Hz

$Et_3P{=}N{-}SiMe_3$ δ -15.73, ^2J(PSi) 22.0 Hz
$Ph_3P{=}N{-}SiMe_3$ δ -11.92, ^2J(PSi) 22.0 Hz

^{31}P NMR spectra: Proton-decoupled ^{31}P spectra were obtained from C_6D_6 (30 °C) or $C_6D_5CD_3$ solutions. δ-values (ppm) are given relative H_3PO_4 (85% in water).

3a at 30 °C: δ 54.1, s; at −54 °C: δ 55.9 and 49.0, broadened AB-system. Coalescence temperature −23 °C; E_A 11.4 kcal/mol.

3b at 30 °C: δ 54.0, s; at −80 °C: δ 61.3 and 51.8, broadened AB-system. Coalescence temperature −22 °C; E_A 11.3 kcal/mol.

3c at 30 °C: δ 54.3, s; at −52 °C: δ 56.4 and 48.9, AB, $^2J_{AB}$ 9.1 Hz. Coalescence temperature −20 °C, E_A 11.5 kcal/mol.

3d at 30 °C: δ 53.1, s.

3e at 30 °C: δ 54.4, s. No splitting is observed even at −65 °C.

3f at 30 °C: δ 53.8, s; at −37 °C: δ 56.3 and 48.9, AB $^2J_{AB}$ 12.2 Hz. Coalescence temperature −23 °C, E_A 11.35 kcal/mol.

4d at 30 °C: δ −0.6 and −20, AB, $^1J_{AB}$ 229 Hz

4e at 30 °C: δ −0.7 and −17.4, AB, $^1J_{AB}$ 222 Hz

4f at 30 °C: δ 5.6 and −18.4, AB, $^1J_{AB}$ 232 Hz

4g at 30 °C: δ 4.8 and −14.6, AB, $^1J_{AB}$ 232 Hz

4h at 30 °C: δ 2.4 and −17.8, AB, $^1J_{AB}$ 226 Hz

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