(*N*-lithioamino)diorganophosphanes and Bis(*N*-Lithioamino)organophosphanes: Synthesis and Structures

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Dedicated to Professor Alfred Schmidpeter on the occasion of his 70th birthday

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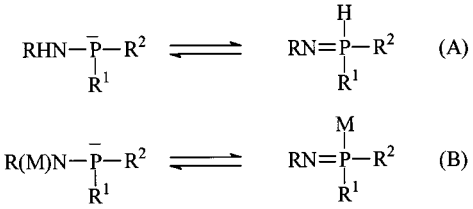
Butyllithium (*n*BuLi) deprotonates Ph_2P–NH*t*Bu in ether to give $(Ph_2P–NLi{t}Bu)_2{\cdot}OEt_2$. There is no Li···P interaction in this molecule. Three compounds of the type $R'P(NLiR)_2$ have been obtained by lithiation of $R'P(NHR)_2$, isolated as $[BuP(NLi{t}Bu)_2{\cdot}OEt_2]_2$, $[PhP(NLiPh)_2{\cdot}OEt_2]_2$ and $[PhP(NLiPh)_2]_2$. Reaction of *n*BuLi with $MeP(NH{i}Pr)_2$ in hexane/THF leads to $[MeP\{N(Li){i}Pr]_2{\cdot}THF\}_4$ with an asymmetric cluster structure comprising one LiP_3, three $LiPN_2$, three LiP_2N and one LiN_3 cluster units. The molecular structures of these compounds as determined by X-ray structure analysis show that they are best depicted as *N*-lithioaminophosphanes and not as the isomeric *P*-lithioiminophosphoranes.

Introduction

The chemistry and particularly the structural chemistry of alkali metal hydrazides has recently been the subject of great interest. They are versatile reagents and offer surprising structural features.[1] Amongst the series $R_2N-N(R)M$, R_2N-NM_2, $R(M)N-N(M)R$, $R(M)N-NM_2$ and M_2N-NM_2 (M = alkali metal), so far only the first three members are known.[1] Furthermore, only very few derivatives with the heavier alkali metals have been described, a typical example being $CsMeN-N(SiMe_3)_2$.[1d] All these metal hydrazides are dimers, trimers or oligomers in spite of the fact that the alkali metal cations coordinate donor solvent molecules. The most significant feature of the hydrazide units is that the two nitrogen atoms are present in a planar or almost planar coordination sphere in which the planes around the N atoms are more or less perpendicularly oriented to one another.

Monoaminophosphanes $R_{2-n}H_nN-PR_2$ are the mixed higher homologues of hydrazines $R_{2-n}H_nN-NR_2$. Upon lithiation, amidophosphanes $RLiN-PR_2$ form.[2] Association of these molecules should preferentially occur by means of intermolecular Li···N interactions, although Li···P interactions may also be present;[2] these should, however, not be preferential due to the softer base character of the phosphorus(III) atom. Moreover, it is well-known that aminophosphanes may be involved in prototropism (A) which can lead to imido-phosphoranes;[3] metallotropism, as described in Equation (B), might therefore also be observable.[2]

As far as aminophosphanes are concerned, the analogy between hydrazines and mono-aminophosphanes can be readily expanded because a P^{III} atom allows for the formation of the series of compounds $RHN-PR_2$, $(RHN)_2PR$ and $(RHN)_3P$ and all these should be amenable to deprotonation. Another extension includes bis(phosphanyl)amines $(R_2P)_2NH$ and their metallation to $(R_2P)_2NM$ compounds (M = Li, Na, K, Cs) where it has been found that for M = Li, a dimeric species with Li–N bonds is formed, while the sodium salt shows only Na–P bonds.[4] Therefore it is interesting, but difficult to predict, what kind of metal–ligand interaction can be expected for bis-metallated di(amino)phosphanes. For this reason we have not only investigated the metalation of monoaminophosphanes[5] but also the bis(amino)organophosphanes. Because tris(amino)phosphanes $P(NHR)_3$[6] (R = Me, *t*Bu, Ch_2Ph, $C_{12}H_{25}$) condense too readily to give cyclophosphazanes $[RHN-P=NR]_2$ or $P_4N_6R_6$, we did not include a study of the deprotonation of tris(amino)phosphanes.



Results

Bis(organoamino)organophosphanes, $R'P(NHR)_2$

Aminophosphanes $R'_{3-n}P(NHR)_n$ bearing primary amino groups are amenable to condensation. This tendency increases with the number of amino groups attached to the phosphorus atom and decreases with increasing bulk of the *P*- and *N*-substituents. The first compound of type $R'P(NHR)_2$ such as $C_5F_5P(NHR)_2$ (R = *t*Bu, CH_2Ph) was reported in 1966.[7] Another series of compounds $PhP(NHR)_2$ (R = Me, Et, *n*Pr, *i*Pr, *t*Bu) was described in 1967.[8] They can be oxidized to $PhP(X)(NHR)_2$ (X = O, S) or alkylated to their phosphonium salts $[PhR'P(NHR)_2]X$[8] which are thermally more stable than

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the parent compounds. Furthermore, bis(arylamino)arylphosphanes seem to be less prone to condensation[9] and, therefore, several bis(anilido)arylphosphanes have been characterized by spectroscopic methods.[9][10] Moreover, the structure of mes*P[NH(mes*)]$_2$ (mes* = 2,4,6-tris-*tert*-butylphenyl = supermesityl) has been determined by X-ray diffraction techniques.[10] Scherer[11] and Payne[8] were able to isolate MeP(NH*t*Bu)$_2$ as the most stable species amongst bis(monoorganoamino)methylphosphanes. Even MeP(NH*i*Pr)$_2$ **(1)**, can be isolated like MeP(NH*t*Bu)$_2$ **(2)** as the product of aminolysis of MePCl$_2$, as described by Equation (1).[8] The aminolysis method has been used to prepare compounds **1** to **5**.

$$R'PCl_2 + 4NH_2R \longrightarrow R'P(NHR)_2 + 2(NHR_3)Cl \quad (1)$$

R'	Me	Me	Ph	Ph	Ph
R	iPr	^{t}Bu	iPr	^{t}Bu	Ph
	1	**2**	**3**	**4**	**5**

$$mesPCl_2 + 2Me_3SiNHR \xrightarrow[\text{toluene}]{20\ ^\circ C} mesP(NHR)_2 + 2Me_3SiCl \quad (2)$$

R = ^{t}Bu, **6**
R = iPr, **7**

$$2\ mes\ P(NHiPr)_2 + H_2O \longrightarrow \textbf{8} + 2\ iPrNH_2 \quad (3)$$

8

$$mesP(NH^tBu)_2 + H_2O \xrightarrow{CH_2Cl_2} mes{-}P(=O)(H){-}NH^tBu + iPrNH_2 \quad (4)$$

9

It is interesting to note that amination of MePCl$_2$ with LiNHR or Me$_3$SiNHR was unsuccessful in our hands. Moreover, aminolysis of MePCl$_2$ with aniline or mesidine to MeP[NH(aryl)]$_2$ was equally unsuccessful; this contrasts with the aminolysis of PhPCl$_2$ which provided the series of bis(organoamino)phenylphosphanes **3**–**5** as shown in Equation (1). While ether is a good solvent for these reactions, toluene is required for the preparation of **5** in order to circumvent solubility problems.

In contrast, the bis(monoorganoamino)mesitylphosphanes **6** and **7** were readily obtained by allowing mesPCl$_2$ (mes = mesityl) to react with aminosilanes Me$_3$Si–NHR as described in Equation (2). However, the formation of **7** was always accompanied by the formation of the di-phosphetidine **8** (Equation 3). The ratio of **7**:**8** before distillation was ≈4:1. Slow hydrolysis of **7** yielded the phosphonic acid amide **9** as described by Equation (4), a compound that was not obtained by direct hydrolysis of **7**.

NMR Spectra

Chemical shifts for ^{31}P and ^{15}N NMR, as well as coupling constants, of compounds **1**–**8** are summarized in Table 1 and additional data (^{1}H, ^{13}C) are reported with the individual compounds in the Experimental Section.

Table 1. Chemical shifts ^{31}P and ^{15}N and P-N coupling constants for bis(organoamino)organophosphanes **1**–**8** and related compounds measured in C_6D_6

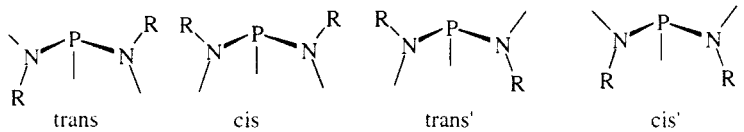
	δ^{31}P	δ^{15}N	^1J(P-N) (Hz)
MeP(NH^{i}Pr)$_2$ **(1)**	51.7	−302.1	65.3
MeP(NH*t*Bu)$_2$ **(2)**	39.2	−289.9	65.7
PhP(NH*i*Pr)$_2$ **(3)**	58.9	−304.8	67.9
PhP(NH*t*Bu)$_2$ **(4)**	42.0	−292.2	68.2
PhP(NHPh)$_2$ **(5)**	46.8	−294.6	66.4
mesP(NH*i*Pr)$_2$ **6**	58.7	−303.5	63.4
mesP(NH*t*Bu)$_2$ **7**	44.1	−298.9	59.9
[mesP−N*i*Pr]$_2$ **8**	242.0	−374.1	t 37.5
mes*P(NHmes*)$_2$	82	–	–

mes* = 2,4,6-tris-*tert*-butylphenyl.

All compounds exhibit a single ^{31}P NMR signal, and the ^2J(P-C) coupling constants were calculated from the satellites. Shielding of the P nucleus increases from 12.5 to 16.9 ppm by replacing *i*Pr groups with *t*Bu groups, and this difference decreases in the series R = Me > mes > Ph. On the other hand, the nitrogen nuclei are better shielded by *i*Pr groups than by *t*Bu groups. The shift differences are $\Delta\delta(^{15}N)$ = 12.2 for the pair **1** and **2**, 12.6 for the pair **3** and **4,** but only 4.6 for the pair **6** and **7**.

Both, ^{1}H and ^{13}C NMR spectra of all bis(isopropylamino)phosphanes **1**, **3** and **6** show nonequivalent CH$_3$ groups with different ^3J(H-H) coupling due to the prochirality of the *i*Pr groups. The corresponding signal for the CH proton is a multiplet of higher order. On the other hand, four ^{13}C NMR signals for the phenyl group reveal free rotation about its P–C bond.

There are two signals for the NH protons of bis(isopropylamino)phenylphosphane which are fairly broad. These signals do not stem from a doublet due to coupling of the protons with ^{31}P because the two signals did not collapse into a single line on ^{31}P decoupling, nor were they affected by proton decoupling. This is in contrast to the observation by Payne et al.[8] who found for their compounds that the NH signals collapsed to a singlet on irradiation at the frequency of the methine proton implying ^3J(H-H) coupling. On the other hand, there are also two NH signals in compound **4** where there is no methine proton available for a ^3J(H-H) coupling. On heating, a [D$_8$]toluene solution of **3** led to coalescence of the two NH signals at 80 °C, while all other ^{1}H NMR signal remain unchanged. A $^{13}C\{^1H^{31}P\}$ double resonance experiment clearly demonstrates that two doublets for the CH*Me*$_2$ groups are due to ^3J(P-C) because this gives rise to two singlets. Thus, the temperature-dependence of the NH proton signals suggests hindered rotation about the P–N bond. However, there was no indication of hindered rotation in the *tert*-butylaminophosphane **6**, although the steric requirement of the *tert*-butyl group would certainly be more demanding than that of the prochiral isopropyl group. However, the height of the rotational barrier has not been determined experimentally



A **B** **C** **D**

Two ^{1}H and ^{13}C NMR signals for the isopropyl groups were also observed in the cyclophosphazane **8**, appearing as doublets in the ^{1}H NMR spectrum due to ^{3}J(H-H) coupling. In addition, the *O*-methyl groups of the mesityl substituents are also not magnetically equivalent, which also became apparent for the *m*-H atoms which appear as two signals and, therefore, also indicated hindered rotation. The four-membered ring structure of **8** was ascertained by NMR spectroscopy, with a triplet for the ^{15}N NMR signal due to coupling to the P atoms [^{1}J(P-N) = 37.5 Hz], as well as by its molecular weight, and finally, by an X-ray structure analysis.

Ab initio Calculations

Hindered rotation about the P−N bond of bis(organoamino)organophosphanes may result in chirality at the phosphorus center. As depicted in formulae **A**−**D**, four different rotamers result as limiting cases. The conformers **A** and **C** are chiral, while **B** and **D** are achiral due to a plane of symmetry.

In order to obtain information on compound **3**, our best-studied bis(amino)phenylphosphane, single point calculations were performed. A simulation of the NMR spectrum of **3**, taking its solid state structure into account, must consider 19 spins (^{1}H, ^{15}N, ^{31}P). This would be technically quite demanding. Therefore, we turned to NBO analysis as implemented in the Gaussian 94 program package,[12] and Figure 1 depicts calculated Mulliken charges and Wiberg bond orders. The latter renders bond orders usually as too large.

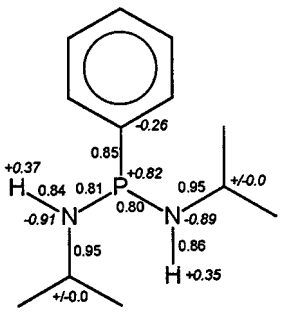


Figure 1. Wiberg bond orders and Mulliken charges for PhP(NH*i*Pr)$_2$

In spite of this, P−N bond order values of ≈ 0.80 correspond to a single bond, and calculated negative charges are associated with the nitrogen centers as well as the *ipso* carbon atoms. Positive charges are centered at the P atom and the hydrogen atoms. This implies localized pairs of electrons at the P and N centers. Surprisingly, the lone pair at the P atom resides in an orbital close to sp^3 while the lone pairs at the nitrogen atoms are of *p*-type, resulting from an almost planar environment of the substituents at the nitrogen atoms. This result already excludes any discussion that a hindered rotation about the P−N bond originates from π-bonding. Taking the molecular parameters into account, as obtained from the X-ray structure determination (see below), single point calculations (basis set 31G*) have been performed by rotating one isopropyl amino group by 360° leaving the rest of the molecular structure untouched. The result of these calculations is depicted in Figure 2.

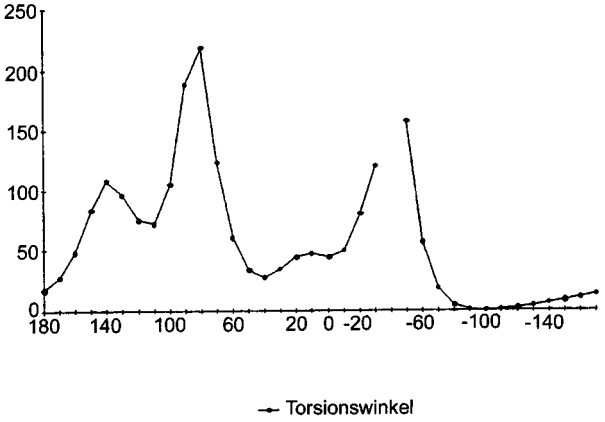
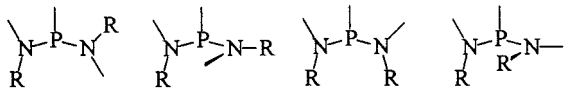


Figure 2. Rotational barrier calculated for PhP(NH*i*Pr)$_2$, using its structural data as found for the solid state; one isopropyl group was kept fixed, the second one was rotated about its P−N bond



E **F** **G** **H**

As can be seen, there are four minima on the hypersurface corresponding to the following rotational angles: −100°, 130°, 40° and 0°. The corresponding conformations are shown by structures **E**−**H**. At a torsion angle of −50°, the isopropyl groups overlap. In going from a *cis*- to a *trans*-structure, an energy of 200 kcal mol^{-1} is required. This barrier cannot be surpassed at ambient temperature. On the other hand, a cogwheel rotation of both isopropyl groups will most likely lower this barrier significantly.

Crystal and Molecular Structures

The molecular structures of two primary bis(amino)phosphanes were determined by X-ray structure analysis. PhP(NH*i*Pr)$_2$ **3**, crystallizes as needles in the orthorhombic

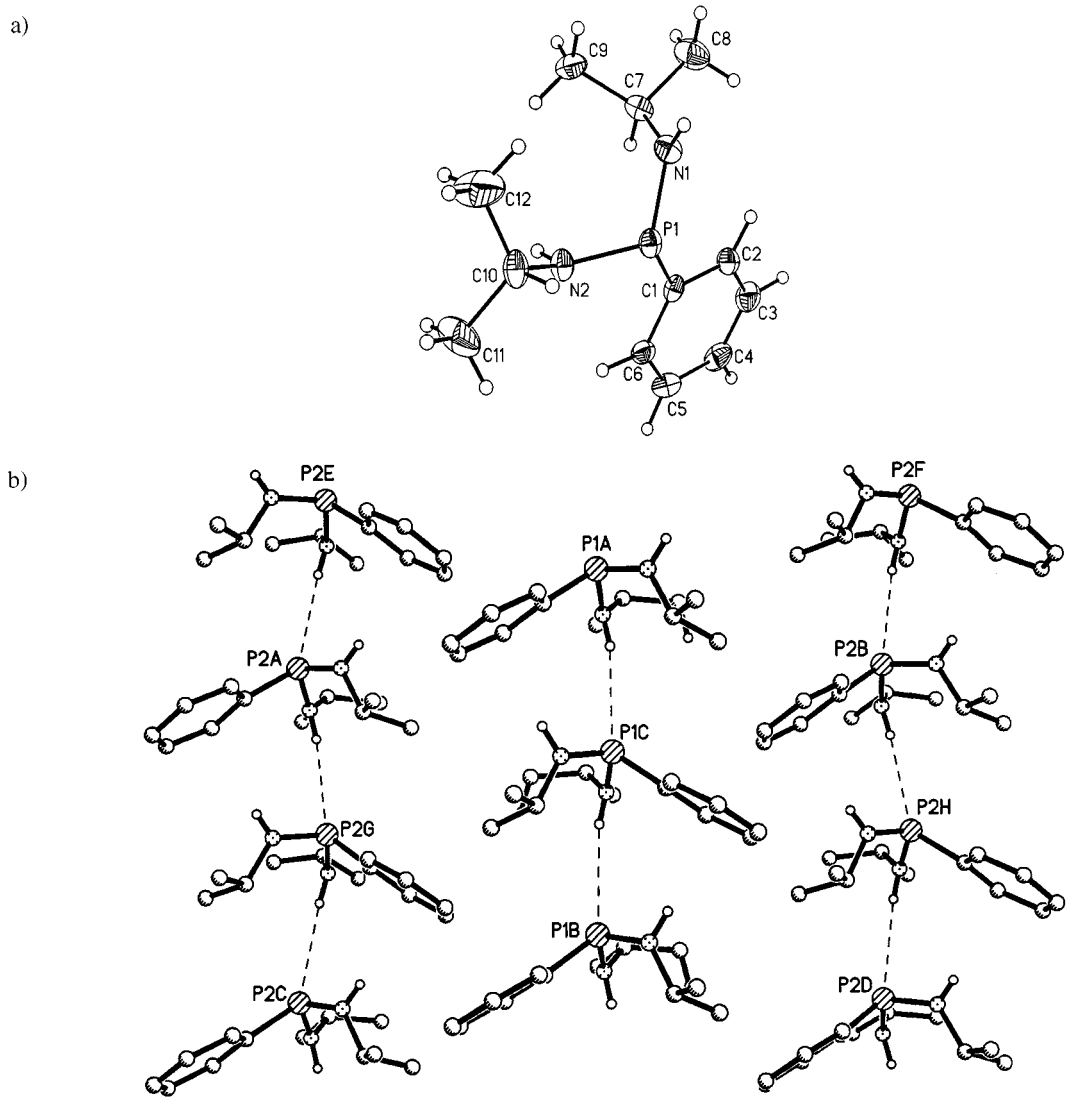


Figure 3. a) The molecular structure of the two independent $PhP(NHiPr)_2$ molecules in ORTEP representation; thermal ellipsoids are drawn on a 25% probability scale; selected bond lengths (Å) and angles (°): P1−N1 1.687(4), P1−N2 1.875(4). P1−C1 1.844(5), N1−C7 1.448(7), N2−C10 1.476(6); − N1−P1−N2 113.7(2), N1−P1−C1 100.2(2), N2−P1−C1 99.2(2), C10−N2−P1 120.1(4), C7−N1−P1 127.9(4); P2−N3 1.674(5), P2−N4 1.684(5), P2−C13 1.836(5), N3−C19 1.471(6), N4−C22 1.465(7); N3−P2−N4 113.0(2), N3−P2−C13 99.6(2), N4−P1−C22 100.0(2); b) Stereoplot of the contents of the unit cell of $PhP(NHiPr)_2$ **1**, along the b−axis; N3−H3 0.88 Å, H3···P 1.99 Å; angle N3−H3−P2 172.6°

system, space group $Pca2_1$ with $Z = 8$. Therefore, there are two independent molecules in the asymmetric unit, (see Figure 3a). Both molecules differ only slightly in bond lengths and possess almost the same conformation. However the pyramidalization at the P atoms is significantly different as shown by the sum of bond angles at atom P1 (325.9°) and atom P2 (319.7°). Each of these independent molecules are arranged in the unit cell by forming chains resulting from N−H···P hydrogen bonding as shown in Figure 3b.

The N atoms deviate only slightly from a planar environment because the sum of bond angles for N1 is 355.4°, for N2, 352.5°, for N3, 355.4° and for N4, 352.1°. The plane of the phenyl group does not stand perpendicular to the respective N_2P plane but is twisted against it by ≈ 65°. Association of the molecules results from weak hydrogen bonding between N and P atoms of neighboring molecules with a N1(X)···P1(X) distance of 3.789 Å and a N2(X)···P2(X) distance of 3.740 Å. The respective P···H distances are 2.98 and 2.87 Å, and the P−H−N angles are 160.1° and 172.6°, respectively.

In contrast to $PhP(NHiPr)_2$ whose amino groups are present in an *anti*-conformation, a *syn*-conformation is found for $PhP(NHPh)_2$ **5** in the solid state as shown in Figure 4. This compound crystallizes in the centrosymmetric monoclinic space group *Cc*; the molecule itself, however only shows C_1 point group symmetry.

The sum of bond angles at the P1 atom (300.7°), and those at the N atoms (N1: 360°, N2: 358°) are indicative of sp^2 hybridization. An interplanar angle of the phenyl group bonded to atom P1 with respect to the PN_2 plane is 73.5°; so the latter plane is not bisected. As a consequence, the

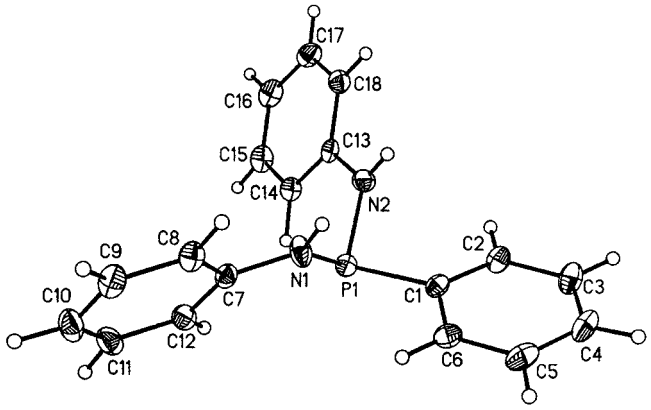


Figure 4. ORTEP representation of a molecule of $PhP(NHPh)_2$ **5**, in the crystal; thermal ellipsoids are drawn on the 25% probability level; bond lengths (Å): P1−N1 1.695(2), P1−N2 1.708(2), P1−C1 1.828(2), N1−C7 1.401(3), N2−C13 1.399(3), N1−H1 0.83, N2−H2 0.81; bond angles (°): N1−P1−N2 105.4(1), N1−P1−C1 97.6(1), N2−P1−C1 97.7(1), P1−N1−C7 127.7(1), P1−N2−C13 126.0(2), H1−N1−P1 118, H2−N2−P1 115

interplanar angles between the C1−C6 phenyl plane with respect to the other two phenyl planes are 62.3° (C7−C12) and 121.2° (C13−C18), respectively, and it should be noted that the phenyl groups of the aniline units are practically in plane with the respective CNH planes (2.6°, 2.4°) allowing for good π-overlap with the π-system of the phenyl groups. This can also be deduced from the short C−N bonds.

In contrast to compound **3**, no NH···P or NH···N hydrogen bonds are present in the crystal of **5**. This may be due to the pronounced pyramidal geometry at the P center and the near planarity of the nitrogen atoms with their phenyl rings resulting in π-interaction. Thus $PhP(NHPh)_2$ is a true molecular compound in the solid state.

As indicated, slow hydrolysis of $mesP(NHiPr)_2$ **7** led to the mesitylphosphonic acid amide mesP(O)H(NH*i*Pr), **9**. Its structure was determined by X-ray methods. The molecule crystallizes in the centrosymmetric monoclinic space group $P2_1/c$. Figure 5a depicts the molecule. Association of the molecules in the solid state can occur by means of NH···P, NH···O and NH···N bonding as well as, but less likely, by PH···O or PH···N bonding. Figure 5b, which shows four molecules, demonstrates that an intermolecular interaction occurs by means of NH···O hydrogen bonding with an intermolecular N···O atom distance of 2.665 Å and an N−H···O bond angle of 175.1°.

The molecular structure of the cyclophosphazane **8** (see Figure 6) is another example of the less preferred *trans*-conformation of the substituents in a centrosymmetric structure.[13] Its bonding parameters fall into the same range as observed for many other derivatives with a P_2N_2 ring. Due to steric effects, the mesityl groups are perpendicular to the P_2N_2 ring. Moreover, the ring nitrogen atoms are slightly pyramidal (sum of bond angles 351.5°). This is a stronger deviation from planarity than usually observed for *trans*-diazadiphosphetidines (358−360°)[14] and is probably a result of the bulky mesityl group.

N-Lithioaminophosphanes

Synthesis

It is to be expected that *N*-lithioaminophosphanes are better nucleophiles than the parent aminophosphanes and therefore might be useful reagents for the synthesis of new ring and chain compounds based on N−P−N structural units. Besides this aspect, the question as to whether these *N*-metallated bis(amino)phosphanes will be present as *N*-metal aminophosphanes or as *P*-metaliminophosphoranes requires the determination of their structures. According to ab initio calculations by Ashby and Trinquier[15] the $RN-PR_2^-$ isomer is favored over the $RN=PR_2^-$ isomer. The stabilization of the latter requires strongly eletronegative substituents such as F or CF_3 bonded to the P atom. Anions of type $RN=PR_2^-$ can probably only be detected if the Li counter ion is separated from the anion by complexation or if replaced by a non-coordinating cation. Otherwise one has to expect association of the *N*-lithioaminophosphanes which raises the question as to whether this will occur through the N or/and P atoms. Indeed, compounds **10**−**14** are associated in the solid state as revealed by X-ray structure determinations.

However, NMR spectroscopic data of these compounds in solution usually showed more ^{31}P NMR signals than expected; even when the solutions had been prepared from well defined crystalline material. This suggests that several solution species are formed from the dimeric and tetrameric species. Therefore, the ^1H and ^{13}C NMR spectra were complex, and it is quite evident that a detailed study of the NMR spectra is required to characterize the solution state of compounds **10**−**14**. So far, this has not yet been achieved successfully.

Metallation of $mesP(NHtBu)_2$ with *n*BuLi yielded no $mesP[N(Li)tBu]_2$ but the *P*-butyl derivative **11**. Therefore, *n*BuLi not only deprotonated the aminophosphane but also induced an exchange of the *P*-bonded organo group.

Reactions

The *N*-lithio derivatives of bis(amino)organophosphanes are expected to be versatile reagents particularly for the synthesis of new heterocycles. Here we describe only a single example as a prototype, namely the synthesis of a 1,3-diaza-2-phospha-4,5-diboretidine **15**.

This new heterocycle can be considered to be a 6π-electron system provided that the P atom resides in a planar moiety. However, the X-ray structure (vide infra) clearly disproves this because the P atom is pyramidal. Nevertheless, this example demonstrates that many other new heterocyclic systems will be accessible via the new reagents, and we will report on these later.

Crystal and Molecular Structures

Compound **10** crystallized at −30°C from its ether solution in the monoclinic space group *C*2/*c*. It proved to be

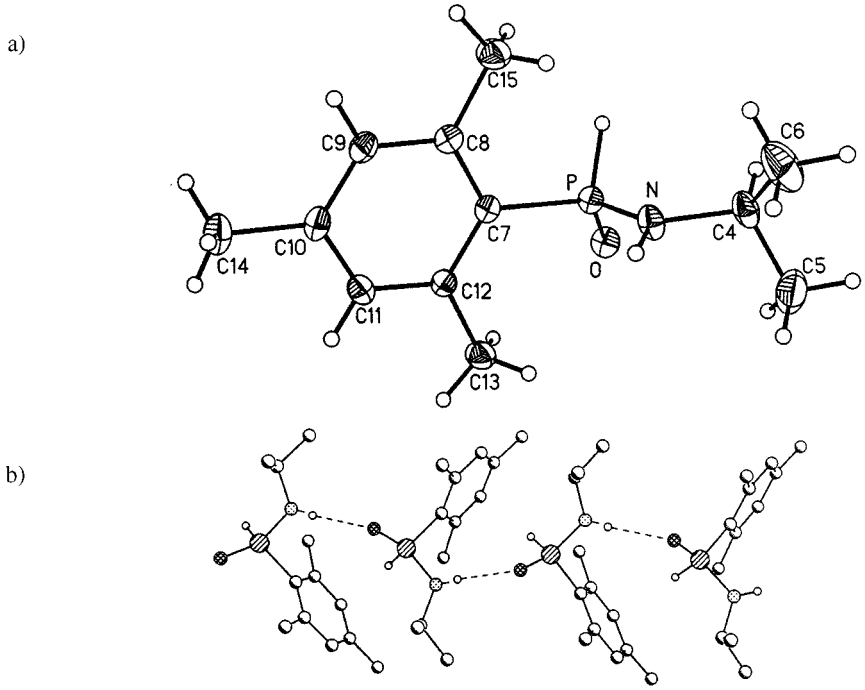


Figure 5. a) Molecular structure of mes−P(O)H(NH*i*Pr) **(9)** in the crystal; thermal ellipsoids are represented on a 25% probability scale; selected bond lengths (Å): P1−N1 1.618(2), P1−O 1.484(2), P1−C 1.808(2), P1−H 1.28(1), N − H2 0.75(1); bond angles (°): O−P1−N1 118.3(1), N1−P1−C7 102.8(1), O−P1−C7 115.9(1), H1−P1−N1 104.3, H1−P1−O 108.7, C7−P1−H1 105.6; b) Association of the molecules **9** via N−H···O interactions; the chains are oriented along the c axis; intermolecular distance O···H: 2.13(1) Å, O···H−N bond angle: 175.1°

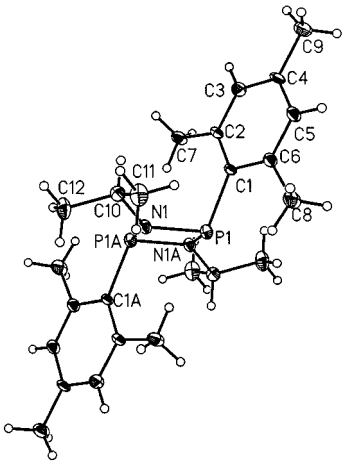


Figure 6. Molecular structure of the diazadiphosphetidine **8**; thermal ellipsoids are depicted on a 25% probability limit; selected bond lengths (Å): P1−N1 1.741(3), P1−N1A 1.727(3), P1−C1 1.852(4), N1−C10 1.463(4); bond angles (°): N1−P1−N1a 81.5(1), N1−P1−C1 106.51), C1−P1−N1a 108.6(1), P1−C1 C6 114.8(3), C10 N1 P1a 125.7(2), C10 N1 P1 127.3(2); interplanar angle: C1 to C6/P_2N_2 94.0; torsion angle: C10−N1−P1−N1a−148.8°

$[Ph_2P–N(Li)tBu]_2{\cdot}OEt_2$ **10**

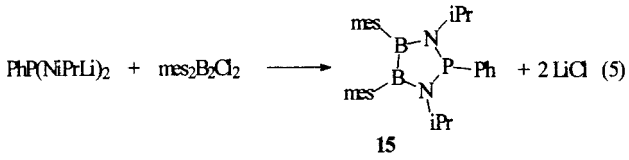
$\{BuP[N(Li)tBu]_2\}_2{\cdot}2OEt_2$ **11**

$\{PhP[N(Li)tBu]_2\}_2$ **12**

$\{PhP[N(Li)Ph)_2\}_2{\cdot}4OEt_2$ **13**

$\{MeP[N(Li)iPr]_2\}_4$ **14**

the hemietherate of $[Ph_2P-N(Li)tBu]_2$ whose molecular structure is depicted in Figure 7. The molecule shows a crystallographically imposed C_2 point group symmetry.



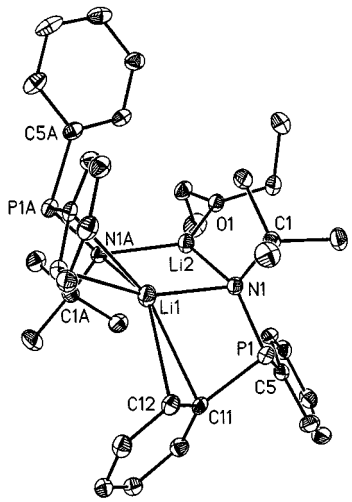


Figure 7. ORTEP representation of the molecular structure of **10** in the crystal; hydrogen atoms are omitted for clarity; thermal ellipsoids are drawn on a 25% probability level; selected interatomic distances (Å): Li1−N1 2.018(5), Li2−N1A 2.075(5), Li2−O1 2.034(7), P1−N1 1.686(3), P1−C5 1.848(3), P1−C11 1.849(3), N1−C1 1.504(4); bond angles (°): C5−P1−C11 99.7(1), C5−P1−N1 112.6(2), C11−P1−N1 103.0(1), P1−N1−Li1 106.9(2), P1−N1−Li2 139.4(1); other interatomic distances (Å): Li1···C11 2.700(3), Li1···C12 2.602(6), Li2···C2 2.602(6); Li1···P1 2.983(2), Li1···Li2 2.42(1); torsion angle C1−N1−P1−N1a −148.8°

Because the structure of $Ph_2P-NHtBu$ is still unknown, no direct comparison of **10** to changes in bonding parameters with the parent compound can be made. The P−N bonds of **10** are shorter than in $Ph_2P-NHmes$ [1.730(2)Å][16] but not as short as in $Ph_2P-NmesLi\cdot 2OEt_2$ [1.661(2) Å]. Only the nitrogen atoms are involved in coordination with the Li atoms. The Li−N bond to the ether-bearing Li atom is 0.057 Å longer than the Li−N bond to the ether-free atom Li1. However, this atom has two close contacts with H atoms of two methyl groups. Moreover, atom Li1 is also shielded sterically by the two phenyl groups as there are four η-Li−C interactions. These are sufficient to prevent the addition of an ether molecule to the atom Li1, and also to inhibit Li−P coordination. The two phenyl groups are mutually oriented at an interplanar angle of 110.9° to one another, and the coordination of the phenyl groups C11 to C16 and C11a to C16a to the atom Li1 form an interplanar angle of 45.6°. A torsion angle of 15.8° for the four-atom arrangement Li2−N1−C1−C2 reveals an almost optimal orientation for the Li2···H2C and Li2···H10A "agostic" interactions with distances of 2.44 Å. Thus the structure of the anion shows an *anti*-conformation of the substituents at the PN unit (torsion angles C1−N1−P1−C5: −121°, C1−N1−P1−C11: 134°).

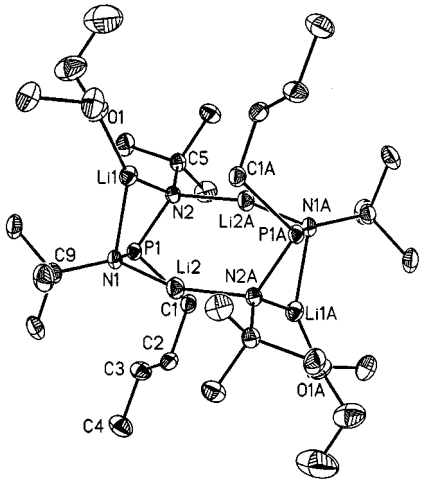


Figure 8. The molecular structure of $\{BuP[N(Li)tBu]_2\}_2\cdot 2OEt_2$ **(11)** in the crystal; hydrogen atoms omitted for clarity; thermal ellipsoids are represented on a 25% probability scale; selected bond lengths and atom distances (Å): Li1−N1 2.034(5), Li1−N2 1.983(5), Li2−N1 1.930(5), Li2−N2a 1.962(5), Li1−O1 1.926(5), P1−N1 1.707(2), P1−N2 1.715(2), P1−C1 1.876(3); P1···Li1 2.543(5), Li2···C5A 2.785(5), Li2···P1 3.046(5); bond angles (°): C1−P1−N1 100.9(1), C1−P1−N2 100.9(1), N1−P1−N2 98.7(1), N1−Li1−N2 80.5(2), O1−Li1−N2 142.7(3), O1−Li1−N1 135.9(2), N1−Li2−N2A 160.0(3), 85.2(2), Li1−N1−P1 85.2(2), Li2−N1−P1 113.6(2), Li1−N2−P1 86.6(2)

The dilithio compound **11** crystallizes as a dimer of composition $BuP[N(Li)tBu]_2\cdot OEt_2$. Its molecular structure is shown in Figure 8. The molecule is centrosymmetric due to a crystallographically-imposed center of inversion at the center of an eight-membered ring. The two non-equivalent P−N bonds are slightly but significantly different and somewhat longer than in **10**. They can be considered as P−N single bonds. All nitrogen atoms are involved in coordination to Li atoms. There are two kinds of Li atoms. Atom Li1 is coordinated to one oxygen atom and two N atoms, and the sum of bond angles at the tricoordinated atom Li1 is 359°. In addition, there is a fairly short Li1···P1 contact [2.543(5) Å]. However, this is a consequence of the geometry of the four-membered ring because the lone pair of the atom P1 presumably points outwards from the four-membered butterfly-shaped Li1−N1−P1−N2 ring. Taking the sum of bond angles at P1 (300.5°) into account, one can assume that hybridization at this atom is halfway between p^3 (270°) and sp^3 (330°) so that the lone pair at the P atom no longer has pure s character. While the N1−Li1−N2 bond angle of the four-membered ring is rather sharp [81.5(2)°] the N1−Li2−N2a bond angle is quite open (144.9°). Atom Li2 is, however, sterically shielded by two Li···H interactions ranging from 2.37 to 2.39 Å. While the folding angle of the four-membered ring Li1−N1−P1−N2 is 32.7°, the N1Li1N2 plane adopts an interplanar angle of 85° with the N1Li2N2a plane. Figure 9 shows the closest intramolecular Li···H contacts (2.4−2.7 Å) of molecule **11** which contribute to the steric shielding

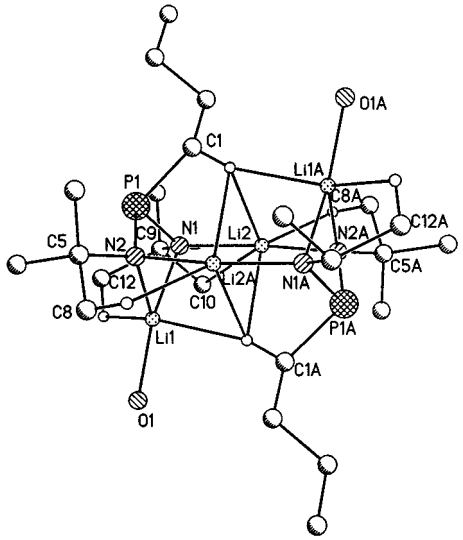


Figure 9. View almost along the Li_2N_4 plane on the structural core of molecule **11** including short H−Li contacts

of the Li atoms. A structure similar to **11** is observed for the solvent-free centrosymmetric molecule $\{PhP[N(Li)-tBu]_2\}_2$ **12**, as shown in Figure 10. There are two independent "monomers" in the asymmetric unit. The dimeric molecules exhibit eight-membered Li_4N_4 rings with the P atoms bridging adjacent pairs of N atoms, or, alternatively, two N_2PLi four-membered rings are connected by two Li atoms, with the formation of a total of four Li−N bonds.

Two Li centers are η^6-coordinated to phenyl groups. As a result of this coordination, the Li2−N2−Li1 bond angle is only 93.3° (100.1° in **11**), and the interplanar angle N1−Li1−N2/N2−Li2−N1a is now 99.1°. Moreover, the folding angle between the N_2Li and the N_2P plane of the four-membered ring is 16.5°, and, therefore the ring is closer to planarity than the analogous ring in **11**. As ex-

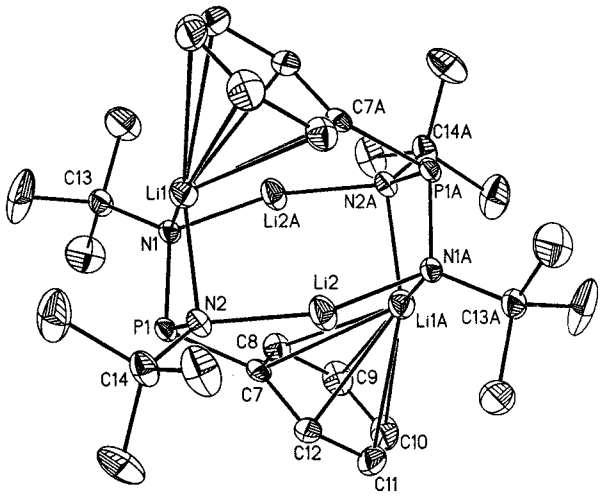


Figure 10. The structure of the molecule **12** in the crystal; hydrogen atoms are omitted for clarity and thermal ellipsoids are represented on a 25% probability scale; selected bond lengths and atom distances (Å): Li1−N1 2.017(5), Li1−N2 2.027(6), Li2−N2 1.918(5), Li2−N1a 1.928(6), P1−N1 1.686(3), P1−N2 1.693(2), P1−C7 1.867(3), Li1···P1 2.559(5), Li1···C 2.618−2.750(6); bond angles (°): N1−P1−C7 100.8(1), N2−P1−C7 99.8(1), N1−P1−N2 102.8(1), N2−Li2−N1a 149.9(2), N1−Li1−N2 81.5(2), Li1−N2−Li2 93.3(2), P1−N1−Li2A 115.8(2), P1−N1−Li1 87.0(2), P1−N2−Li1 86.5(2), P1−N2−Li2 119.6(2); interplanar angles: N2−Li2−N1A/C7−C12 44.3, N2−Li2−N1a/N1−P1−N2 71.4, N2−Li2−N1A/N1−Li1−N2 99.1

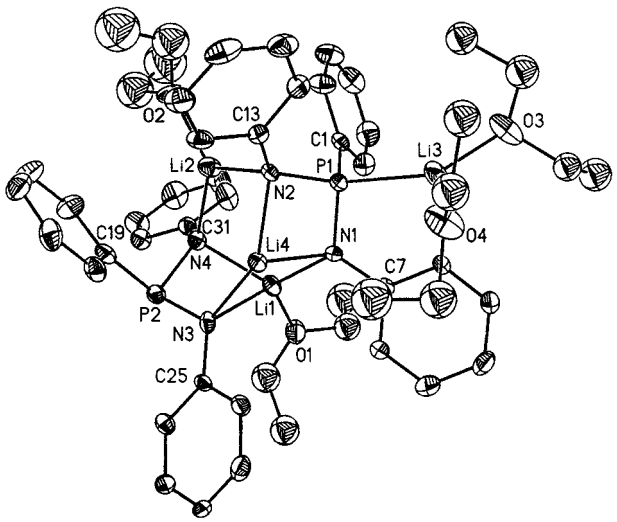


Figure 11. ORTEP molecular structure of $\{PhP[N(Li)Ph]_2 \cdot 2OEt_2\}_2$ **(13)**; hydrogen atoms are omitted for clarity; thermal ellipsoid are drawn on a 25% probability scale; selected bond lengths and atom distances (Å): Li1−N1 2.09(1), Li1−N4 2.09(2), Li1−N3 2.26(2), Li1−O1 1.89(1), Li2−N2 2.03(1), Li2−N4 2.01(1), Li2−O2 1.90(1), Li3···P1 2.55(2), Li3−O3 1.88(1), Li3−O4 1.91(1), Li4−N1 2.08(2), Li4−N2 2.01(1), Li4−N3 1.95(1), P1−N1 1.688(6), P1−N2 1.683(7), P2−N3 1.711(7), P2−N4 1.704(7), P1−C1 1.84(1), P1−C19 1.839(9), P1···Li4 2.64(1), P1···Li3 2.55(2), L2···Li1 2.746(9), P2···Li4 3.097(8); bond angles (°): N1−P1−N2 99.3(3), N1−P1−C1 104.7(4), N2−P1−C1 104.3(4), N3−P2−N4 97.6(3), N3−P2−C19 100.2(4), N4−P2−C19 101.9(4), O3−Li3−O4 114.1(8), O3−Li3−P1 126.9(9), O4−Li3−P1 118.9(8), O1−Li1−N1 117.0(7), N1−Li1−N4 118.7(7), O1−Li1−N4 119.6(7), N2−Li2−N4 116.1(7), O2−Li2−N2 118.2(7), O2−Li2−N4 125.7(8), N2−Li4−N3 140.7(7), N1−Li4−N2 78.0(5), N1−Li4−N3 110.7(6), P1−N1−Li4 88.3(7), P1−N1−Li1 125.3(7), Li1−N1−Li4 71.6(8), P1−N2−Li4 90.8(8), P1−N2−Li2 116.1(6), Li2−N2−Li4 89.0(8), P2−N3−Li4 115.2(7), P2−N3−Li1 86.7(7), P2−N3−C25 119.3(7), P2−N4−Li1 92.3(8), P2−N4−Li2 116.6(7), P2−N4−C31 118.3(8), Li1−N4−Li2 102.3(9)

pected for a four-membered LiN_2P ring, a short Li···P distance of 2.559(5)Å is observed.

Although compound **13** is formally related to both **11** and **12**, as it is a dimeric dimetallated bis(monoorganoamino)organophosphane (see Figure 11), its structure turned out to be vastly different to **12**, obviously due to solvation by diethyl ether. There is (formally) one ether molecule per Li atom. However the structure determination revealed that there are altogether *four* different Li centers, one of which binds two ether molecules, two others only one, while the fourth Li center carries no ether molecule at all as seen in Figure 11.

There are two molecules of **13** in the asymmetric unit of the triclinic unit cell of space group $P\bar{1}$. The differences between their bonding parameters are insignificant therefore only one molecule is depicted in Figure 11. Formally, the structure can be described as $[(Et_2O)_2Li]$-$[Li_3(NPh)_4(PPh)_2\ OEt_2]$, and the anionic cage as being built from two PN_2Li four-membered rings joined by two LiN bonds to result in a structure of three condensed four-membered rings whose open faces are bridged by a $Li(OEt_2)$ unit by two nitrogen atoms. On the other hand, the $(Et_2O)_2Li$ unit is joined to atom P1 with a comparatively short Li−P distance of 2.54 Å while the Li4−P1 distance in the four-membered ring is 0.1 Å longer. In contrast, the four-membered ring P2N3N4Li1 is characterized by a longer and therefore weaker Li1−N3 interaction, and this causes a lengthening of the Li1−P2 distance to 2.746(5)Å.

P−N bonds to atom P1 are shorter than in the parent compound $PhP(NHPh)_2$, but are of equal lengths, while those at atom P2 seem to be slightly different but are on average only 0.01 Å longer than those at P1. These bonds correspond to those found for $PhP(NHPh)_2$.

The lithiation of $MeP(NH\textit{i}Pr)_2$ led to $MeP[N(Li)\textit{i}Pr]_2$ which turned out to be the *tetramer* **14**, crystallizing with 5 molecules of THF. Four of these THF molecules are bonded to Li centers, the fifth remains uncoordinated in the triclinic lattice. Thus the composition of compound **14** can be described as $\{MeP[N(Li{\cdot}THF)\textit{i}Pr]\ [N(Li)\textit{i}Pr]\}_4$ THF but it is surprisingly asymmetric as depicted in Figure 12.

Inspection of Figures 12 and 13 reveals that the Li atoms are coordinated quite differently. While Figure 12 gives an overview of the structure, Figure 13 represents more clearly its cage structure. Atoms Li2, Li4 and Li6 are tricoordinated by two N atoms and one O atom; they form a rhombus with another Li atom which coordinates to the two N atoms. Atoms Li1 and Li7 have three nitrogen atoms as coordination partners and these are arranged in a plane including the Li atoms (sum of bond angles 359.9 and 360° respectively). Two of the N−Li−N angles subtending at Li are comparatively small, ranging from 100.5 to 113.5°.The others are rather wide (144.8 and 149.6°). On the other hand, atom Li3 has two nitrogen atoms and a phosphorus atom as coordination partners. The same number of bonded atoms are observed for atom Li5 which is, however,

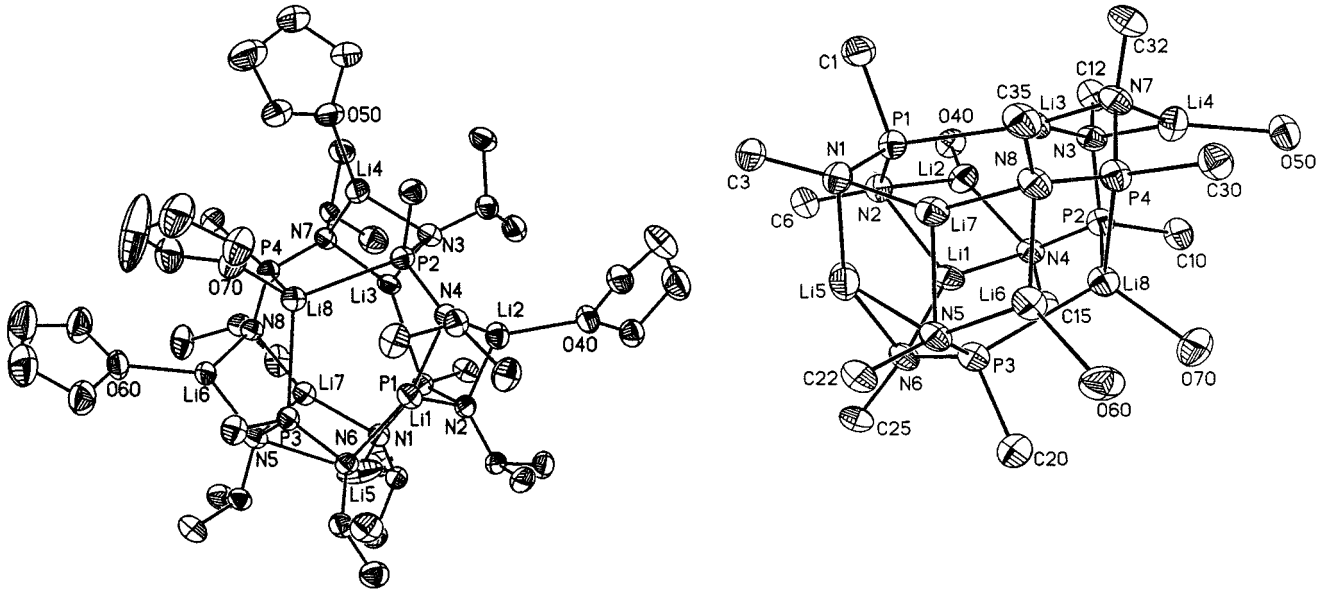


Figure 12. a) ORTEP molecular structure of {MeP[N(Li)*i*Pr]2·thf}$_4$ **(14)**; hydrogen atoms are omitted; thermal ellipsoids are represented at a 25% probability level; selected bond lengths and atom distances (Å): P1−N1 1.671(4), P1−N2 1.683(4), P1···Li3 2.514(8), P1···Li5 2.76(2), P1···Li7 2.854(8), P2−N3 1.677(5), P2−N4 1.686(4), P2···Li8 2.656(9), P3−N5 1.687(4), P3−N6 1.674(4), P3···Li8 2.629(9), P4−N7 1.656(5), P4−N8 1.682(4), P4···Li8 2.677(9), C1−P1 1.871(7), N1−Li5 1.96(2), N1−Li7 2.082(9), N2−Li1 2.17(1), N2−Li2 2.043(9), N3−Li3 2.006(9), N3−Li4 2.05(1), N4−Li1 2.105(9), N4−Li2 1.97(1), N5−Li6 1.999(9), N5−Li7 2.17(1), N6−Li1 2.03(1), N6−Li5 1.96(1), N7−Li3 2.004(9), N7−Li4 1.98(1), N8−Li6 2.01(1), N8−Li7 2.036(9); bond angles (°): N1−P1−N2 112.5(2), Li3−P1−N2 107.5(2), Li3−P1−N1 121.5(2), C1−P1−N1 105.1(2), C1−P1−N2 108.7(2), N2−Li1−N4 10.5(4), N2−Li1−N6 113.6(4), N4−Li1−N6 144.8(5), P1−N1−Li5 68.1(2), P1−N1−Li7 98.4(2), Li5−N1−Li7 80.3(6), P1−N2−Li2 112.2(3), P1−N2−Li1 102.9(3), Li1−N2−Li2 72.2(4),N2−Li2−N4 111.1(5), N2−Li2−O40 123.0(4), N4−Li2−O40 116.1(4), C10−P2−N4 105.2(2) C10− P2−N3 106.2(3), C10−P2−Li8 118.6(3), N3−P2−N4 109.4(2) Li8−P2−N3 107.3(3), Li8−P2−N4 109.8(2), P2−N3−Li3 103.9(4), P2−N3−Li4 96.6(4), P2−N4−Li1 105.8(3), P2−N4−Li2 104.7(4), C20−P3−N5 109.9(2), C20−P3−N6 105.6(3), N5−P3−N6 111.3(2), P3−N5−Li6 110.8(3), P3−N5−Li7 104.4(3), P3−N5−Li5 72.6(3), P3−N6−Li5 91.3(5), P3−N6−Li1 96.3(3), C30−P4−N7 103.0(3), C30− P4−N8 104.8(2), N7−P4−N8 116.7(2), C30−P4−Li8 121.6(3), P4−N7−Li4 109.9(4), P4−N8−Li7 107.9(3), P4−N8−Li6 99.7(3), N3−Li3−N7 107.1(4), N3−Li3−P1 118.5(4), N7−Li3−P1 134.3(4), O50−Li4−N7 128.8(5), O50−Li4−N3 125.1(5), O50−Li4−P2 107.8(4), N1−Li5−N6 148.5(7), N1−Li5−P3 120.7(5), O60−Li6−N5 124.0(6), O60−Li6−N8 128.1(5), O60−Li6−P4 117.0(4), N1−Li7−N5 109.9(4), N1−Li7−N8 149.6(6), N5−Li7−N8 160−4(5), O70−Li8−P3 109.1(5), O70−Li8−P2 109.8(3), O70−Li8−P4 109−2(4), P2−Li8−P3 111.3(3), P2−Li8−P4 110.3(4); b) The core structure of **14** was obtained by removing all the substituents from the N and P atoms and the C atoms of the THF molecules

not part of a Li_2N_2 rhombus. Finally, atom Li8 binds to three phosphorus atoms and one oxygen atom. Li8 represents the only Li center which is tetracoordinated. Amongst the tricoordinated Li centers, atoms Li2 and particularly Li5 are unusual because the sum of bond angles at Li2 is 350° but for Li5 only 323° (without including a possible weak Li5−P3 interaction (2.605(4).Å). One may see this atom as being dicoordinated, particularly because the Li2−N5 distance is 2.551(6) Å and the N6−Li5−N1 bond angle is rather open [148.5(7)°]. Similar angles are also observed in the structures of **11** and **12**.

The five-membered ring of the 1,3,2,4,5-diazaphosphadiboretidine **15** is almost planar (sum of bond angles 539.8°). It contains a pyramidal P1 atom, and planar N and B atoms. The B−N bond lengths are characteristic of π-bonds. The B−B bond length is typical for a single bond and lies in the usual range for diborane(4) derivatives. The two mesityl groups include an interplanar angle of 64°.

Discussion

The stability of primary bis(amino)organophosphanes depends on the steric shielding at the P center. This is an indication that the elimination of RNH_2 from these molecules to form, e.g. 1,3,2,4-diazadiphosphetidines[13][14] occurs by intermolecular steps. An intramolecular amine elimination to form an iminophosphane RP=NR′ followed by dimerisation could be an alternative. This process, however, might be less influenced by steric effects. An intramolecular process should be dependent on the conformation of the $R'P(NHR)_2$ molecules. It is evident that a mechanistic study is required to settle this question.

The synthesis of the bis(organoamino)organophosphanes is readily achieved by aminolysis of the respective chloride $R'PCl_2$ or by silazane cleavage. The latter method is versatile and quite useful, particularly if steric effects are not too pronounced.

As demonstrated for $P(NHPh)_3$ ($\delta^{31}P = 73.8$)[6f] the ^{31}P nucleus is better shielded in compound $PhP(NHPh)_2$. Replacement of an *i*Pr group by a *t*Bu group at the N atom also results in a better shielding of the ^{31}P nucleus by 14 ppm. It is also surprising that the ^{31}P nucleus is better shielded in $PhP(NHPh)_2$ than in $PhP(NHiPr)_2$. This may be due to the larger N−P−N bond angle in $PhP(NHiPr)_2$ relative to $PhP(NHPh)_2$, due to a higher s-character of the P atom in $PhP(NHPh)_2$. However, this may be due to the longer P−N bond lengths resulting from hydrogen bonding but we have not determined the degree of association in

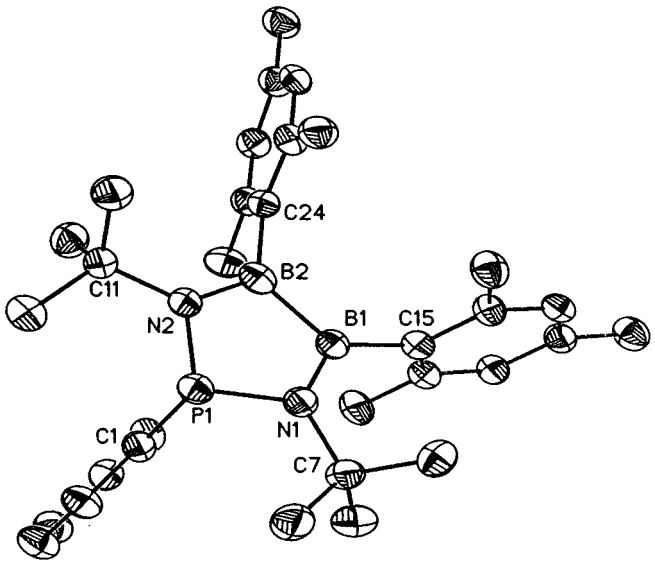


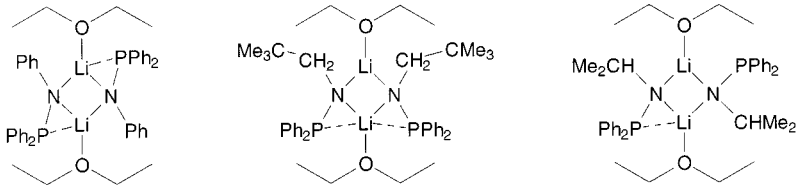
Figure 13. The molecular structure of **15** in the solid state; thermal ellipsoids are represented at a 25% probability level; hydrogen atoms are omitted for clarity; selected bond lengths (Å): P1−N1 1.743(5), N1−B1 1.436(7), B1−B2 1.71(1), B2−N2 1.428(7), N2−P1 1.732(5), P1−C1 1.841(6), B1−C15 1.585(8), B2−C24 1.605(8); bond angles (°): C1−P1−N12 100.9(2), C1−P1−N2 101.5(2), N1−P1−N2 95.7(2), P1−N1−B1 114.8(4), P1−N1−C7 115.7(3), C7−N1 B1 129.4(5), N1−B1−B2 106−6(4), N1−B1−C15 125.3(5), B1−B2−N2 108.4(5), B1−B2−C24 128.1(5), B2−N2−P1 114.3(4); torsion angle: C1−P1 N1−C7 −80.4°; interplanar angle: N1N2P1/C1 to C6 92.8°; C15 to C20/C24 to C29 71.1°

solution. On the other hand, there is only a small variation both in the shielding of the ^{15}N nuclei as well as in the coupling constant ^{1}J(P-N), irrespective of the substituent at the P atom (Me, Ph, mes) or the N atoms (*i*Pr, *t*Bu, Ph). This suggests that in solution the structural differences observed for the structure of $PhP(NHiPr)_2$ and $Ph(NHPh)_2$ in the solid state, particularly with respect to the pyramidal geometry at the P atom, but also at the N atoms, becomes less significant or even negligible. This also holds for the mesityl bis(amino)phosphanes, although the coupling constants ^{1}J(P-N) are noticeably smaller (by 4.5 and 8.3 Hz, respectively, for the isopropyl and *tert*-butyl derivative), probably due to steric effects particularly for the sterically-crowded $mesP(NHtBu)_2$.

It would be most interesting to compare the structural parameters and their changes in the aminophosphanes with those of the respective *N*-lithio compounds. Unfortunately there are, at the moment, too few pairs of compounds to be compared in this respect. Nevertheless, the structural aspects of *N*-lithioaminophosphanes are attracting increasing interest [2,4,15,16] since the determination of the X-ray structure of $[Ph_2P-NPh(Li\cdot OEt_2)]_2$.[2] So far, $Ph_2P-N(Li)mes^*\cdot 2OEt_2$[16] is the only monomeric *N*-lithio-monoaminophosphane known which shows a *trans*-conformation with respect to the P−N bond. A related compound is the lithium salt of the bis(diphenylphosphanyl)amine $Ph_2P-NH-PPh_2$.[4] Therefore, bulky groups are necessary besides supporting ligands such as THF or Et_2O which coordinate to the Li centers. The *trans*-conformation in monoaminophosphanes inhibits any intramolecular P···Li interaction. However, this kind of interaction is observed in $Ph_2P-N[Li(THF_3)]-PPh_2$ where a *cis*-conformation was determined, a result also supported by ab initio calculations.[4a] Besides these two structurally-characterized compounds, there are three dimeric *N*-lithioaminophosphanes of type $Ph_2P-N(Li\cdot OEt_2)R$ (formulae **I**−**L**) where the *cis*-conformation prevails. These compounds exhibit different degrees of P···Li interactions.[16] Thus, **I** and **K** show weak Li···P interactions, while there is only a single one in **L**. Thus an increasing steric effect due to the nitrogen substituents decreases the probability of Li···P interactions. These conclusions are supported by the molecular structure of **10** where a *trans*-conformation is observed for the $Ph_2P-NtBu$ unit which inhibits a Li···P interaction. The *trans*-conformation results from the N−Li coordination, and the η^6-coordination of two phenyl groups of two different $Ph_2P-NtBu$ units. The consequence of this is, in addition, that only a hemietherate is formed. The P−C bond lengths in **11** are similar to those in **6** and **L**, a situation that does not allow one to draw the conclusion as to whether the orbitals at nitrogen mix with the P−C* orbitals or not.[15][16]

For dimetallated bis(amino)organophosphanes, structures different to monometallated monoaminodiorganophosphanes are to be expected. It is, however, somewhat surprising that out of the four examples investigated, three are dimeric. Of these, two have rather similar structures in spite of the fact that **11** is an ether solvate and **12** is non-solvated. Moreover, the formation of **11** was also not expected because the nucleophilic exchange of *P*-bonded organo groups is an exception in phosphorus chemistry. This kind of reaction has been observed, for instance, in the reaction of tris(2-pyridinyl)-trimethylsilylamino-phosphoranes with methyl lithium.[17] Since this exchange of R groups has only been observed during the metallation of $mesP(NHtBu)_2$ and not of phenyl-bis(monoorganoamino)-phosphanes it appears that the mesityl group acts as a better leaving group than a phenyl group. Thus the butyl anion not only acts as a base for NH deprotonation, but also as a nucleophile, attacking the P^{III} center.

The conformation of the $CP(NC)_2$ units in **11** and **12** can be considered as representing a *trans* conformation with dihedral C−P−N−C angles of −122.2° and 102.2° for **11** and −126.1° and 123.2° for **12.** Four-membered LiN_2P rings are formed which are connected by two Li−N−Li bonds, making all nitrogen atoms tetracoordinated. Although the Li···P distances in **11** and **12** are 2.543 and 2.559 Å, respectively, and are therefore shorter than the "secondary" Li−P bonding in **I,** the short distances are certainly a consequence of the geometry of the four-membered ring, and reflect no Li−P single bond interaction. The rather sharp N−Li−N bond angle (80.5° in **11** and 81.5° in **12**) is also an indication that Li−P bonding is avoided. However, the N−P−N bond angles are 98.7 and 102.8° in **11** and **12**. In addition, the lone pair of electrons at the P atoms cannot be of an s-type because the sum of bond angles at these atoms is 291° and 303.4°, respectively. There is only a change of 2.7° for the N−P−N bond angles in **12**, com-



I **K** **L**

pared to the non-metalated aminophosphane, and only a slight elongation of the P−N bond lengths (average 0.01 Å), which has to be considered as almost negligible. However, the P−C bond length in **12** is 0.05 Å longer than in **11,** and this is an indication of a negative hyperconjugative effect.[8,15,16] Most interesting is the presence of dicoordinated Li atoms both in **11** and **12**, a situation that is similar to that found in tetrameric lithium tetramethylpiperidine[10] or trimeric $LiN(SiMe_3)_2$.[18] Another feature of **12** is that two of its Li centers are η^6-coordinated to phenyl rings. This mode of coordination saturation does not occur very often, but is nevertheless not uncommon,[19] and found, for instance, in $[(Me_3Si)_2N-N(Li)Ph]_4$[1d] or $[Ph(Li)N-N(Li)SiMe_3]_4$[1c] the latter also containing $(\eta^6\text{-}C_6H_5)_2Li$ units.

No η^6-PhLi groups are present, however, in $\{PhP[N(Li)Ph]_2\}_2 \cdot 4OEt_2$, **(13)**. The rather unsymmetrical structure of this compound having four different kinds of Li centers is unique. Once again there is a Li···P distance (2.55 Å) across a LiN_2P ring that might indicate weak bonding, but we regard this as a consequence of the ring structure. One may also look upon this molecule as a contact ion pair because one Li atom is not used for completing the $Li_3P_2N_4$ cage. The Li−P atom distance of this unique Li center, formally a $(Et_2O)_2Li^+$ unit, is 2.64 Å. This distance is similar to that found in lithiumphosphides,[20] e.g. [(TMEDA·Li)PPh_2 (2.61 Å)][21] or $[LiP(SiMe_3)_2]4\cdot 2THF$ (2.48−2.64 Å).[22] While the P−N bond lengths at the atom P2 are not influenced by the metallation, obviously because the P atom remains tricoordinate, the P−N bonds at P1, the atom which can be considered as tetracoordinated become shorter. This is unusual insofar as an increase in coordination normally causes bond lengthening. Therefore, this can be taken as an indication of π-bonding in the P−N bond, as supported by the observation that the P−C bond length is not affected and remains the same as in **12**.

Even more unsymmetrical is the structure of **14**. The most interesting feature is the presence of a P_3LiO unit besides a planar N_3Li unit. By maximizing the number of Li−N contacts, it is obvious that one LiN_3 unit must finally lead also to Li−P contacts. The first principle leads to three four-membered Li_2N_2 rhombi, a structural unit typical for lithium amides.[19] Of the eight Li centers, seven are tricoordinate, and only the Li atom of the LiP_3 unit becomes tetracoordinated by also binding a THF molecule. Although one can rationalize that Li−N contacts in lithiated aminophosphanes are preferred as a result of the principle of hard/soft acid-base character, LiP interactions cannot be totally avoided particularly in the lithiated bis(amino)phosphanes $[R'P(NLiR)_2]_n$ for n > 2. Due to the association of the lithiated aminophosphanes, the question as to whether these might contain the structural unit of a *P*-metallated iminophosphorane can be discarded, as there is no indication of short P−N bonds (higher bond order) where Li···P coordination is observed. It is evident that bis-metallated bis(amino)phosphanes have structures completely different to bis-metallated hydrazines. The reason that they must have different geometries is due to their composition, which is $RP(NLiR)_2$ for the former and R(Li)N−N(Li)R for the latter with the P atom offering at least potentially, an additional coordination site

Experimental Section

All experiments were performed under anhydrous conditions with standard Schlenk techniques and nitrogen as the protecting gas. Solvents were dried by standard procedures, distilled under a nitrogen atmosphere and stored under N_2. The amines and the phosphorus halides used were commercial products, whose purity was checked by NMR methods. $Ph_2P-NHtBu$ was prepared as described in the literature.[2] − M.p.′s were determined with a Mel-Temp apparatus. − Elemental analysis was performed at the institute′s microanalytical laboratory. − NMR: Jeol 270, Jeol 400 with $SiMe_4$ or C_6D_6 internal standard for ^1H and ^{13}C, internal 1M aqueous $^{15}NH_4^+$ solution for ^{15}N, 85% H_3PO_4 internal for ^{31}P; 1M LiCl solution external for ^7Li. − IR: Nicolet FT 320 (samples in Nujol/Hostaflon mulls); MS: Atlas CH7. − X-ray: Siemens P4 diffractometer equipped with a CCD area detector and LT2 low temperature device; Mo-K_α radiation, graphite monochromator.

Bis(isopropylamino)methylphosphane (1): $iPrNH_2$ (14.7 g, 249 mmol) was dissolved in diethyl ether (250 mL) and a solution of $MePCl_2$ (5.84 g, 50.3 mmol) in ether (50 mL) was added at 0°C while stirring. A precipitate formed. Stirring was continued overnight, the solid was removed by filtration, and washed three times with 150 mL of ether. The solutions were combined, and the solvent and excess amine were removed in vacuo. The residue was then subjected to distillation. Yield: 6.3 g of **1** (78%), colorless oil b.p. 52°C/2 Torr. − ^1H NMR (C_6D_6, 400 MHz): δ = 0.9 (d, $^3J_{HH}$ = 6.4 Hz, 6 H, CH−CH_3), 1.0 (d, $^3J_{HH}$ = 6.4 Hz, 6 H, CH−CH_3), 1.1 (d, $^2J_{PH}$ = 5.8 Hz, 3 H, P−CH_3), 1.6 (s, broad, 2 H, N*H*), 3.1−3.2 (m, 2 H, C*H*−CH_3). − ^{13}C NMR (C_6D_6, 100 MHz): δ = 18.7 (d, $^1J_{PC}$ = 2.8 Hz, P−CH_3), 26.4 (d, $^3J_{PC}$ = 6.0 Hz, CH−CH_3), 26.9 (d, $^3J_{PC}$ = 3.7 Hz, CH−CH_3), 44.7 (d, $^2J_{PC}$ = 12.6 Hz, *C*H−CH_3). − ^{15}N NMR (C_6D_6, 27.4 MHz): δ = −302.1 (d, $^1J_{PN}$ = 65.3 Hz). − ^{31}P NMR (C_6D_6, 81 MHz): δ = 51.7 (s). − $C_7H_{19}N_2P$ (162.22): calcd. C 51.83, H 11.81, N 17.27; found C 49.24, H 11.96, N 16.82.

Bis (*tert*-butylamino)methylphosphane (2): Prepared in a similar manner to **1** from $tBuNH_2$ (17.3 g, 243 mmol) and $MePCl_2$ (5.0 g,

43 mmol) in a total of 200 mL of diethyl ether. Yield: 7.6 g (84%), colorless oil, b.p. 53°C/5 Torr. – ^{1}H NMR (C_6D_6, 400 MHz): δ = 1.1 (d, $^2J_{PH}$ = 6.6 Hz, 3 H, P–CH_3), 1.2 (s, 18 H, C–CH_3), 1.4 (s, broad, 1 H, N*H*), 1.5 (s, broad, 1 H, N*H*). – ^{13}C NMR (C_6D_6, 100 MHz): δ = 23.7 (d, $^2J_{PC}$ = 3.5 Hz, P–CH_3), 32.4 (d, $^3J_{PC}$ = 9.6 Hz, C–CH_3), 50.8 (d, $^2J_{PC}$ = 13.7 Hz, *tert*-*C*). – ^{15}N NMR (C_6D_6, 27.4 MHz): δ = –289.9 (d, $^1J_{PN}$ = 65.7 Hz). – ^{31}P NMR (C_6D_6, 80 MHz): δ = 39.2 (s). – $C_9H_{23}N_2P$ (190.27): calcd. C 56.81, H 12.18, N 14.72; found C 55.72, H 12.07, N 14.01.

Bis(isopropylamino)phenylphosphane (3): Prepared analogously to **1** from *i*PrNH$_2$ (20.9 g, 350 mmol) in ether (250 mL) and PhPCl$_2$ (12.7 g, 70 mmol) in ether (50 mL). Isolated by distillation, b.p. 76–78°C /0.2 Torr as an oily liquid. On standing at 4°C, crystals formed with m.p. 6°C. Yield: 12.6 g of **3** (79%). – ^{1}H NMR (C_6D_6, 400 MHz): δ = 1.0 (d, $^3J_{HH}$ = 6.2, CH-CH_3), 1.1 (d, $^3J_{HH}$ = 6.3 Hz, 6 H, CH–CH_3), 1.7 (s, broad, 1 H, N*H*), 1.75 (s, broad, 1 H, N*H*), 3.2 (m, 2 H, C*H*–CH_3, 7.1–7.7 (m, 5 H, C_6H_5). – ^{13}C NMR (C_6D_6, 67.9 MHz): δ = 26.5 (d, $^3J_{PC}$ = 6.1 Hz, CH–CH_3), 26.8 (d, J_{PC} = 4.1 Hz, CH–CH_3), 46.2 (d, $^2J_{PC}$ = 7.5 Hz, *C*H–CH_3), 127.7 (s, *p*-C_6H_5), 128.1 (d, $^3J_{PC}$ = 4.1 Hz, *m*-C_6H_5), 131.1 (d, $^2J_{PC}$ = 15.3 Hz, *o*-C_6H_5), 148.0 (d, $^1J_{PC}$ = 5.1 Hz, *ipso*-C_6H_5). – ^{15}N NMR (C_6D_6, 27.4 MHz): δ = –304.8 (d, $^1J_{PN}$ = 67.9 Hz). – ^{31}P NMR (C_6D_6, 81 MHz): δ = 58.9 (s). – $C_{12}H_{21}N_2P$ (224.29), calcd. C 64.26, H 9.44, N 12.49; found C 63.72, H 8.94, N 12.47.

Bis(*tert*-butylamino)phenylphosphane (4):[7] Prepared analogously to **1** from *t*BuNH$_2$ (15.0 g, 210 mmol) and PhPCl$_2$ (5.7 g, 32 mmol) in 200 mL of ether. Yield: 5.9 g of **4** (73%), slightly yellow oil, b.p. 98°C/0.8 Torr. – ^{1}H NMR (C_6D_6, 400 MHz): δ = 0.0 (d, $^4J_{PH}$ = 0.5 Hz, 18 H, C–CH_3), 1.5 (s, broad, 1 H, NH), 1.7 (s, broad, 1 H, NH), 6.9–7.3 (m, 5 H, C_6H_5). – ^{13}C NMR (C_6D_6, 100 MHz): δ = 32.7 (d, $^3J_{PC}$ = 8.2 Hz, C–CH_3), 51.1 (d, $^2J_{PC}$ = 16.1 Hz, *tert*-C), 127.2 (s, *p*-C_6H_5), 127.7 (d, $^3J_{PC}$ = 4.2 Hz, *m*-C_6H_5), 130.1 (d, $^2J_{PC}$ = 17.2 Hz, *o*-C_6H_5, 148.0 (d, $^1J_{PC}$ = 3.5 Hz, *ipso*-C_6H_5). – ^{15}N NMR (C_6D_6, 27.4 MHz): δ = 292.3 (d, $^1J_{PN}$ = 68.2 Hz). – ^{31}P NMR (C_6D_6, 81 MHz): δ = 42.0 (s). – $C_{14}H_{25}N_2P$ (252.34), calcd. C 66.64, H 9.99, N 11.27; found C 66.36, H 9.75, N 11.10.

Bis(anilido)phenylphosphane (5): PhPCl$_2$ (4.5 g, 25 mmol) was dissolved in toluene (50 mL), and a solution of aniline (9.3 g, 100 mmol) in toluene (100 mL) was added with stirring in such a manner that the temperature of the resulting suspension never exceeded 25°C. After stirring overnight, the insoluble material was removed by filtration and washed with a total of 100 mL of diethyl ether. (The solution may turn turbid.) The solid was then removed after several hours. The combined solutions were reduced to 30 mL in volume. The remaining solution was layered with pentane. After cooling to 0°C a crystalline solid separated, m.p. 70–72°C. Yield: 3.0 g of **5** (42%). – ^{1}H NMR (C_6D_6, 400 MHz): δ = 4.4 (s, broad, 2 H, N*H*), 6.6–7.7 (m, 15 H, C_6H_5). – ^{13}C NMR (C_6D_6, 100 MHz): δ = 117.0. (d, $^3J_{PC}$ = 11.7 Hz, *m*-C_6H_5), 120.3, s, 128.7 (d, $^3J_{PC}$ = 4.0 Hz, *m*-C_6H_5), 129.0, s, 129.5, s, 130.2 (d, $^2J_{PC}$ = 17.0 Hz, *o*-C_6H_5), 141.7, s, 145.7 (d, $^1J_{PC}$ = 13.8 Hz, *ipso*-C_6H_5). – ^{15}N NMR (C_6D_6, 27.4 MHz): δ = –294.6 (d, $^1J_{PN}$ = 66.4 Hz). – ^{31}P NMR (C_6D_6, 81 MHz): δ = 46.8 (s). – $C_{18}H_{17}N_2P$ (297.32): calcd. C 73.96, H 5.86, N 9.58; found C 72.15, H 5.87, N 9.36.

Bis(*tert*-butylamino)mesitylphosphane (6): Prepared analogously to **7** from mesPCl$_2$ (1.2 g, 5.5 mmol) and *t*BuHN–SiMe$_3$ (3.2 g, 22 mmol) in 30 mL of toluene. Yield: 1.17 g of **6** (4.0 mmol, 72%), b.p. 100°C/0.1 Torr, yellow oil. – ^{1}H NMR (C_6D_6, 400 MHz): δ = 1.2 (s, 18 H, C- CH_3), 2.3 (s, 3 H, *p*-CH_3), 2.2 (s, broad, 1 H, NH), 2.3 (s, broad, 1 H, NH), 2.6 (s, 6 H, *o*-CH_3), 6.8 (s, 2 H, *m*-C_6H_2). – ^{13}C NMR (C_6D_6, 100 MHz): δ = 20.9 (s, *p*-CH_3), 22.5 (d, $^3J_{PC}$ = 21.4 Hz, *o*-CH_3), 32.2 (d, $^3J_{PC}$ = 10.0 Hz, C–CH_3), 51.2 (d, $^2J_{PC}$ = 21.7 Hz, *tert*-C), 129.6 (d, $^3J_{PC}$ = 4.2 Hz, *m*-C_6H_5), 137.4 (s, *p*-C_6H_5), 139.3 (d, $^2J_{PC}$ = 18.7 Hz, *o*-C_6H_5), 140.4 (d, $^1J_{PC}$ = 13.4 Hz, *ipso*-C_6H_5). – ^{15}N NMR (C_6D_6, 27.4 MHz): δ = –298.9 (d, $^1J_{PN}$ = 59.9 Hz). – ^{31}P NMR (C_6D_6, 81 MHz): δ = 44.1 (s). – $C_{17}H_{31}N_2P$ (294.42): calcd. C 69.35, H 10.61, N 9.51; found C 69.06, H 9.70, N 9.32.

Di(isopropylamino)mesitylphosphane (7) and 1,3-Diisopropyl-2,4-dimesityl-1,3,2,4-diazadiphosphetidine (8): A solution of mesPCl$_2$ (1.7 g, 7.6 mmol) in toluene (20 mL) was added to a stirred solution of *i*PrHN–SiMe$_3$ (3.90 g, 29.3 mmol) in toluene (30 mL). The mixture was heated at reflux for 14 h. Me$_3$SiCl and toluene were then stripped off from the clear orange-colored solution. The oily residue yielded 1.7 g of **7** (35 mmol), b.p. 109°C/0.1 Torr. – ^{1}H NMR (C_6D_6, 400 MHz): δ = 1.0 (d, $^3J_{HH}$ = 6.3 Hz, 6 H, CH–CH_3), 1.3 (d, $^3J_{HH}$ = 6.3 Hz, 6 H, CH–CH_3), 2.1 (s, broad, 1 H, N*H*), 2.2 (s, broad, 1 H, N*H*), 2.3 (s, 3 H), 2.6 (s, 6 H), 3.3 (m, 2 H, C*H*CH$_3$), 6.7 (2, 2 H, C_6H_2). – ^{13}C NMR (C_6D_6, 67.9 MHz): δ = 20.8 (s, *p*-CH_3), 22.7 (d, $^3J_{PC}$ = 19.8 Hz, *o*-CH_3), 26.3 (d, $^3J_{PC}$ = 4.6 Hz, CH–CH_3), 26.5 (d, $^3J_{PC}$ = 7.7 Hz, CH–CH_3), 47.8 (d, $^2J_{PC}$ = 32.1 Hz, *C*H–CH_3), 129.5 (d, $^3J_{PC}$ = 3.8 Hz, *m*-C_6H_5), 17.8 (s, *p*-C_6H_5), 139.2 (s, *o*-C_6H_5), 139.4 (d, $^1J_{PC}$ = 17.6.1 Hz, *ipso*-C_6H_5). – ^{15}N NMR (C_6D_6, 27.4 MHz): δ = –303.5 (d, $^1J_{PN}$ = 63.4 Hz). – ^{31}P NMR (C_6D_6, 81 MHz): δ = 58.7 (s). – $C_{15}H_{27}N_2P$ (266.37): calcd. C 67.64, H 10.22, N 10.52; found C 64.75, H 9.90, N 10.11.

From a similar reaction, using (4.0 g of *i*PrHN–SiMe$_3$, 30 mmol), 1.7 g of MesPCl$_2$, 7.6 mmol) in toluene (20 mL), 1.7 g of **7** was obtained by distillation. A non-volatile oil remained which was dissolved in CHCl$_3$ (5 mL). On cooling large red needles of **8** separated, m.p. 155°C. Yield: 0.5 g of **8** (30%). – ^{1}H NMR (CDCl$_3$, 400 MHz): δ = 0.8 (d, $^3J_{HH}$ = 6.4 Hz, 6 H, CH–CH_3), 0.81 (d, $^3J_{HH}$ = 6.4 Hz, 6 H, CH–CH_3), 2.3 (s, mesityl–CH_3), 2.7 (s, mesityl–CH_3), 3.1 (s, mesityl–CH_3), 2.9 (m, 2 H, C*H*–CH_3). – ^{13}C NMR (CDCl$_3$, 100 MHz): δ = 3.4 (d, $^3J_{PC}$ = 7.4 Hz, SiCH$_3$), 25.6 (d, $^3J_{PC}$ = 7.5 Hz, CH–CH_3), 25.8 (d, $^3J_{PC}$ = 7.6 Hz, CH–CH_3), 48.6 (d, $^2J_{PC}$ = 10.9 Hz, CH), 127.1 (d, $^3J_{PC}$ = 2.5 Hz, *m*-C_6H_5), 128.1 (s, *p*-C_6H_5), 130.7 (d, $^2J_{PC}$ = 18.6 Hz, *o*-C_6H_5), 147.2 (d, $^1J_{PC}$ = 20.6 Hz, *ipso*-C_6H_5). – ^{15}N NMR (CDCl$_3$, 27.4 MHz): δ = –374.1 (t, $^1J_{PN}$ = 37.5 Hz). – ^{31}P NMR (CDCl$_3$, 81 MHz): δ = 242.0 (s). – MS (70 eV); *m*/*z* (%): 414 (75) [M$^+$], 371 (5) [M$^+$ – *i*Pr], 295 (100) [M$^{\bullet+}$ – mes], 207 (25) [M$^+$ – mesNP*i*Pr], 149 (35). – $C_{12}H_{30}N_4P_2$ (290.): calcd. C 69.54, H 8.75, N 6.76; found C 68.48, H 8.33, N 6.68.

Mesitylphosphinic Acid *tert*-Butylamide (9): From a solution of **7** in C_6D_6 which was kept in a NMR tube fitted with a plastic cap, a few crystals separated within 5 weeks which were characterized as **9** by X-ray structure analysis only. Attempts to hydrolyze **7** with an ether solution saturated with water gave no **9** on attempts to crystallize the product from benzene.

***N*-Lithio(organoamino)phosphanes**

These compounds were prepared from the (organoamino)organophosphanes Ph$_2$P–NH*t*Bu, MeP(NHR)$_2$, PhP(NHR)$_2$ and MesP(NHR)$_2$ by treating ether or toluene solutions with an equivalent amount of *n*BuLi in hexane at –78°C. The solutions were then kept at reflux for 1 h, reduced in volume and kept at low temperature for crystallization.

Since the crystals deteriorated quite rapidly when the solvent was removed, no elemental analysis was performed. Their composition follows from the crystal structure analysis.

Hemietherate of *N*-Lithio-*N*-*tert*-butylamino-diphenylphosphane (10): Ph$_2$P–NH*t*Bu (540 mg, 2.1 mmol) dissolved in ether (10 mL)

Table 2. Crystal data and data collection parameters

Compound	**3**	**5**	**8**	9	**10**	**11**	**12**	**13**	**14**	**15**
Chem. formula	$C_{12}H_{21}N_2P$	$C_{18}H_{17}N_2P$	$C_{12}H_{18}NP$	$C_{12}H_{20}NOP$	$C_{36}H_{50}Li_2N_2OP_2$	$C_{16}H_{37}Li_2N_2OP$	$C_{14}H_{23}Li_2N_2P$	$C_{52}H_{70}Li_4N_4O_4P_2$	$C_{48}H_{108}Li_8N_8O_5P_4$	$C_{32}H_{45}B_2N_2P$
Form. wt.	224.28	292.31	207.24	225.26	602.60	318.33	264.19	904.32	1056.82	510.29
Cryst. size [mm]	0.2 × 0.28 × 0.47	0.2 × 0.2 × 0.25	0.15 × 0.2 × 0.3	0.2 × 0.2 × 0.3	0.2 × 0.2 × 0.2	0.3 × 0.3 × 0.3	0.28 × 0.33 × 0.47	0.2 × 0.25 × 0.25	0.2 × 0.2 × 0.3	0.1 × 0.2 × 0.2
Cryst. system	Orthorhombic	Monoclinic	Triclinic	Monoclinic	Monoclinic	Monoclinic	Triclinic	Triclinic	Triclinic	Monoclinic
Space group	Pca2(1)	Cc	*P*-1	P2(1)/c	C2/c	P2(1)/n	*P*1bar	*P*1bar	*P*1bar	*P*2(1)/c
a, [Å]	9.142(2)	13.102(5)	7.599(9)	8.085(4)	12.316(7)	10.093(3)	10.110(7)	13.4843(3)	12.786(5)	19.81(2)
b, [Å]	15.954(2)	11.549(4)	8.380(7)	18.767(6)	16.406(9)	10.079(3)	11.720(9)	16.0554(4)	14.124(7)	9.442(6)
c, [Å]	18.981(2)	10.655(3)	10.189(13)	9.541(5)	17.158(9)	21.084(7)	14.727(9)	25.3989(4)	20.037(9)	15.97(2
α, [°]	90	90	79.31(5)	90	90	90	80.04(2)	83.475(1)	77.97(2)	90
β, [°]	90	106.50(1)	81.16(3)	112.17(2)	96.34(2)	94.561(12)	74.53(2)	79.746(1)	78.37(2)	95.48(5)
γ, [°]	90	90	70.15(3)	90	90	90	73.75(1)	82.964(1)	66.88(2)	90
V, [Å^3]	2768.4(8)	1546(1)	597(1)	1341(1)	3446(3)	2138(1)	1605(2)	5346.4(2)	3226(3)	2974(7)
Z	8	4	2	4	4	4	4	4	2	4
ρ(calc), [Mg/m^3]	1.076	1.256	1.153	1.116	1.162	0.989	1.093	1.123	1.088	1.140
μ [mm^{-1}]	0.173	0.173	0.194	0.183	0.156	0.130	0.157	0.126	0.161	0.115
F(000)	976	616	224	488	1296	704	568	1934	1152	1104
Index range	$-1 \le h \le 10$ $0 \le k \le 18$ $-21 \le l \le 21$	$-17 \le h \le 16$ $-14 \le k \le 14$ $-12 \le l \le 12$	$-9 \le h \le 9$ $-8 \le k \le 8$ $-13 \le l \le 12$	$-9 \le h \le 9$ $-14 \le k \le 24$ $-12 \le l \le 11$	$-15 \le h \le 15$ $-21 \le k \le 21$ $-22 \le l \le 22$	$-10 \le h \le 10$ $-10 \le k \le 11$ $-23 \le l \le 23$	$-12 \le h \le 12$ $-15 \le k \le 14$ $-18 \le l \le 18$	$-14 \le h \le 14$ $-16 \le k \le 16$ $-26 \le l \le 24$	$-13 \le h \le 12$ $-18 \le k \le 17$ $-25 \le l \le 25$	$-15 \le h \le 16$ $-10 \le k \le 10$ $-17 \le l \le 17$
2 θ [°]	48.00	57.28	54.44	57.30	59.00	46.52	57.62	43.94	54.78	46.52
Temp, [K]	293(2)	193(2)	213	193	183(2)	183	213	173(2)	193	213
Refl. collected	4535	4282	3154	7483	9970	8744	8926	19811	15578	11800
Refl. unique	4234	2973	1676	2355	3469	2907	4850	10544	8884	3259
Refl. observed (4σ)	3256	2831	1499	1416	2761	2589	2738	6480	4845	2296
R (int.)	0.0598	0.0201	0.0451	0.1124	0.0461	0.0303	0.0501	0.0755	0.0812	0.0922
No. variables	291	258	127	150	296	208	343	1040	679	347
Weighting scheme[a] x/y	0.0396/2.9819	0.0136/0.8099	0.0846/0.6542	0.0386/0.711	0.0001/5.9234	0.0410/2.018	0.0539/1.1681	0.0419/29.9749	0.2310/1.4891	0.1701/2.0266
GOOF	1.078	1.121	1.059	1.097	1.314	1.152	1.107	1.096	1.082	1.097
Final *R* (4σ)	0.0550	0.0298	0.0516	0.0436	0.0696	0.0583	0.0445	0.1134	0.1038	0.0892
Final *wR*2	0.1266	0.0668	0.1534	0.0930	0.1087	0.1297	0.1131	0.2185	0.2684	0.2319
Larg. res. peak [e/Å^3]	0.181	0.118	0.484	0.213	0.337	0.594	0.228	0.522	1.082	0.360

[a] $w^{-1} = \sigma^2 F_o^2 + (xP)^2 + yP$; $P = (F_o^2 + 2F_c^2)/3$.

was treated at −70°C with 1.4 mL of a BuLi solution in hexane (2.2 mmol). After refluxing and volume reduction to ca. 1/3, crystals were grown at −30°C, and selected at this temperature for X-ray crystal structure analysis. NMR (supernatant solution): ^{31}P NMR (ether, 81 MHz): several signals in the range δ = 43.6−55.9, − ^{7}Li NMR (77.8 MHz): δ = 1.4 (s, broad).

Dimeric Bis(*N*-lithio-*tert*-butylamino)butylphosphane (11): mesP(NH*t*Bu)$_2$ (0.34 g, 1.7 mmol) dissolved in 10 mL of ether was metallated with 2.24 mL of a 1.56 M solution of *n*BuLi in hexane. The yellow solution was reduced under vacuum, and was kept for 3 weeks at −30°C for crystallization. Clear yellow crystals of **11** had then separated. NMR (supernatant solution): ^{31}P NMR (ether/hexane, 81 MHz): δ = 96.9 (s), 93.6 (s), 89.6 (s) − ^{7}Li NMR (77.8 MHz): δ = 2.5 (s, broad), 2.2 (s, broad).

Dimeric Bis(*N*-lithio-*tert*-butylamino)phenylphosphane (12): PhP(NH*t*Bu)$_2$ (990 mg, 3.9 mmol) dissolved in toluene (30 mL) was metallated with *n*BuLi in hexane (5.2 mL, 8.27 mmol). The yellow solution was reduced to ≈ 10 mL. Yellow crystals grew at −30°C. Yield: 900 mg of **12** (86%). NMR (supernatant solution): ^{31}P NMR (C_6D_6, 81 MHz): δ = 94 (s). − ^{7}Li NMR (77.8 MHz): δ = −2.3 s, 1.4 (s, broad), 2.2 (s, broad).

Dimeric Bis(*N*-lithioanilino)phenylphosphane bis(ether) (13): PhP(NHPh)$_2$ (690 mg, 2.4 mmol) dissolved in ether (20 mL) was metallated at −78°C with *n*BuLi (3.2 mL, 4.96 mmol) in a hexane/ether mixture (3.2 mL hexane, 5 mL ether). A solid formed which dissolved on heating. Yellow crystals of **13** separated from the yellow solution at −30°C. NMR (supernatant solution): ^{31}P NMR (ether, 81 MHz): several signals in the range of δ = 16−88.2 (m). − ^{7}Li NMR (77.8 MHz): δ = −0.2 (s, broad), 1.1 (s, broad), 1.7 (s, broad), 2.8 (s, broad).

Tetrameric Bis(*N*-lithio-isopropylamino)methylphosphane-tetrahydrofuran (14): MeP(NH*i*Pr)$_2$ (830 mg, 5.1 mmol) in THF (20 mL) was treated with *n*BuLi (6.71 mL, 10.8 mmol). A clear yellow solution formed on heating at reflux. Crystals separated at −30°C. Yield: 910 mg of **14** (72%). NMR (supernatant solution and crystals): ^{31}P NMR (C_6D_6, 81 MHz): several signals in the range δ = 24.0 to 39, main signal at 26.5 (m, *J* = 68.5 Hz). − ^{7}Li NMR (77.8 MHz): δ = 1.7 (s, broad).

X-ray Structure Determinations

Crystals from the solutions were transferred at about −30°C in precooled perfluorether oil, and single crystals were selected. The selected crystal was quickly mounted on the tip of a glass fiber and then rapidly transferred to the goniometer head flushed with a gas stream of N_2 cooled to −90°C. The crystal quality was checked by reflection profiles. The unit cell dimensions were calculated from the data on 4 different sets of data of 15 frames each recorded at different φ and χ angles, by rotating φ by 0.3°. Having obtained satisfactory results, data collection was started (10s exposure per frame, 1480 frames collected in the hemisphere mode). Data were reduced by the program SAINT.[23] No absorption correction was applied. The structures were solved by direct methods (SHELXL programs[24]) and non-hydrogen atoms were given anisotropic thermal parameters. Although most H positions could be detected, these were calculated and refined with a riding model and isotropic U_i adopted to U_{eq} of the respective carbon atom. It should be noted that the refinement of the structure of compounds *N*-lithioamidophosphanes **12**, **13**, and **14** converged at comparatively high *R* values. This is due to the fact that the crystal quality was not an optimum, leading also to rather high R_{int} values; moreover the diffracting power was not excellent, e. g. there were only few

reflection at $2\Theta > 40°$ with $I > 3\sigma(I)$. Several crystals of these compounds had been measured without improving the result. Table 4 contains relevant information on the crystallographic data and structure refinement. Additional material (without structure factor tables) are deposited with the Cambridge Crystallographic Data Centre as supplementary publication numbers CCDC 102 977 to 102 986. Copies of the data can be obtained on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, U. K. by quoting the authors, the journal citation [Fax: (internat.)+44-1223/336-033; E-mail: deposit@ccdc.cam.uk].

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