# Synthesis and Characterization of Lithium Complexes of 2-(Diphenylphosphanylamino)pyridine and *N*,2-Bis(diphenylphosphanyl)benzeneamine

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**Keywords:** Lithium complexes / (Diphenylphosphanylamino)pyridine / *N*,2-Bis(diphenylphosphanyl)benzeneamine / Hard-soft interactions / *N*,*N*-chelation / *N*,*P*-chelation / X-ray diffraction

Lithium complexes of 2-(diphenylphosphinoamino)pyridine and *N*,2-bis(diphenylphosphanyl)benzeneamine have been synthesized from the corresponding neutral compounds. In the former complex, the metal ion is coordinated to both nitrogen atoms, forming a constrained four-membered ring, whereas the latter complex forms a five-membered ring as the metal ion coordinates preferentially to the phosphorus atom. Coordination of the metal ion in both complexes is dictated primarily by soft–hard interactions and, subsequently, by the constrained geometry of the ring formed. Both lithium complexes and the corresponding neutral compounds have been characterized by single-crystal X-ray diffraction.

## Introduction

Alkali metal salts play an important role in advanced organic and organometallic transformations.[1] The most extensively used salts contain lithium because this metal cation has the highest charge density of all alkali-metal cations, and inorganic and organic lithium compounds are reasonably soluble in organic solvents.[2] Over 95% of natural products syntheses employ at least one lithium-containing species.[3] *N*-Lithiated species, a very important family in organic chemistry, are the favorite bases in forming ketone enolates,[4] generating low steady-state concentrations of some relatively unstable carbanions,[5] and in preparing heterocyclic thiazenes that incorporate an RC(=N−)N< moiety using lithium amidinates.[6] They are also the main synthons used to introduce an amido group to either early or late transition metal complexes.[7] Since the bonding in these lithium complexes is ionic, the solid-state structures are highly dependent on the steric and electronic properties of the substituents at the anionic center. In addition, the presence of coordinative solvents reduces the high tendency of organolithium compounds to self-assemble into higher aggregates.[3,8]

In the last decade lithium complexes containing *N*,*N*- and *P*,*N*-ligations have attracted much attention. Representative examples of these ligations (Scheme 1) are amidinate,[9] β-diketiminate,[10] pyridylamine,[11] diaminobenzene,[12] phosphanamide,[13] phosphane *Janus Head*,[14] phospha-amidinate,[15] and amidophosphane.[16]

Recently, we have shown that lithium benzamidinates can form dimeric and trimeric species, depending on the solvent,[17] and that the coordination of TMEDA (tetramethylethylenediamine) to lithium benzamidinates guarantees the formation of mononuclear species.[18] These lithium complexes are useful reagents for the bidentate chelation of main group, early- and late-transition metal centers that produce, in some cases, homogeneous complexes as catalysts for the stereoregular polymerization of α-olefins.[18,19]

In the lithium benzamidinate/TMEDA complex the metal ion is coordinated symmetrically by both nitrogen atoms of the benzamidinate moiety, forming an $\eta^2$-ligation and, with the two nitrogen atoms of TMEDA, a tetrahedral environment (Figure 1).

With pyridylamine and amidophosphane ligations $\eta^2$-coordination to the metal ion is normally observed since both heteroatoms (P or N) are located *ortho* to the lithiated position of the aromatic ring (aminobenzene or pyridine), forming a "single side arm coordination". In such coordination there is still space for donor solvent coordination and, commonly, the dimer four-membered ring is the favorite aggregation state.[20]

A basic conceptual question regards the coordination of the alkali metal ion in non-symmetrical systems where, as well as a hard atom (N), the competitive chelation of additional soft and/or hard atoms is also possible. Two systems were selected for this study. The first asymmetric ligation contains the N−C−N−P backbone in which the cen-

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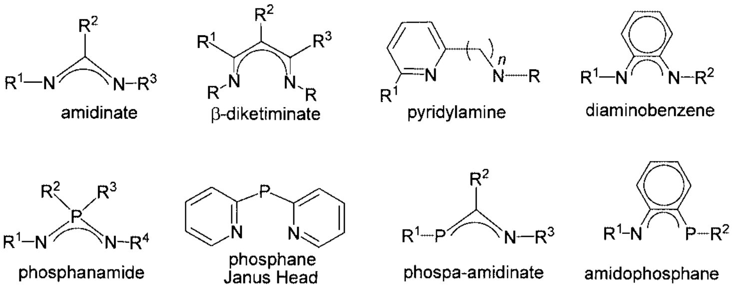


Scheme 1. Representative *P*,*N*- and *N*,*N*-ancillary ligations in lithium complexes

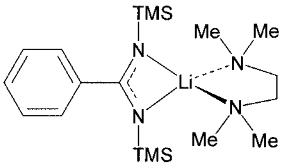


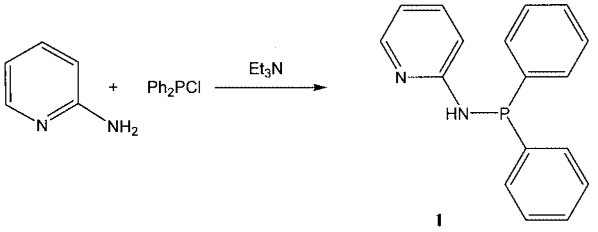
Figure 1. Lithium benzamidinate complex with TMEDA ligation

tral nitrogen atom belongs to a pyridine ring, whereas the second asymmetric system includes a P−C−C−N−P backbone in which the C−C moiety is part of an aromatic ring.

Regarding the former system, only one known structure contains an N−C−N−P moiety in which the nitrogen atoms are attached to a lithium ion and the phosphorus atom is part of a P−N−P−N cyclobutane moiety.[21] Interestingly, 13 structures are known in which an *ortho*-amidopyridinium moiety is anchored to a lithium center, although without the presence of soft (phosphane) atoms.[22,11] Regarding the latter system, structures of late transition metal complexes anchoring the ligand to the metal ion by one or two phosphane P atoms are known but no crystal structure has been reported for alkali or early transition metals of this unsymmetrical ligation.[23] We present here the solid-state characterization of lithium complexes for both N−C−N−P and P−C−C−N−P backbones. To compare the effect of the alkali center, crystallographic parameters of the neutral systems are also described.

## Results and Discussion

2-(Diphenylphosphanylamino)pyridine (**1**) was prepared according to a published procedure[23b] and recrystallized before use [Equation (1)]. X-ray diffraction (Figure 2, Table 1) shows that **1** is a dimeric polymorph that crystallizes in a different space group to the structure known in the literature[23b] although with almost identical bond lengths and angles.



(1)

Lithium complex **2** was prepared quantitatively from the reaction of the neutral compound **1** with butyllithium (1:1)

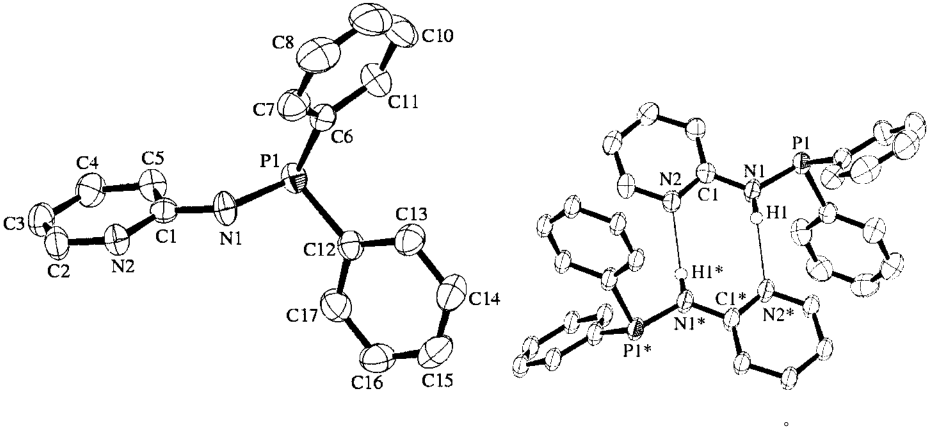
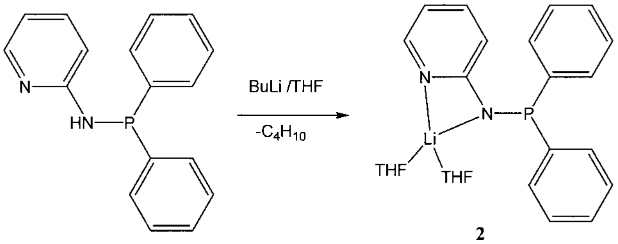


Figure 2. Crystal structure of complex **1** and its dimer in the crystal structure (N1−N2* = 3.050 Å and H1−N2* = 2.18 Å); thermal ellipsoids given at 50% probability

Table 1. Comparison of bond lengths [Å] and angles [°] for complexes **1**−**4**

| Compound **1** | | Complex **2** | | Compound **3** | | Complex **4** | |
|---|---|---|---|---|---|---|---|
| P(1)−N(1) | 1.695(3) | P(1)−N(2) | 1.676(3) | P(2)−N(1) | 1.699(2) | P(2)−N(1) | 1.681(2) |
| N(1)−C(1) | 1.391(4) | N(2)−C(25) | 1.355(4) | N(1)−C(18) | 1.402(3) | N(1)−C(18) | 1.386(3) |
| N(1)−H(1) | 0.8700 | | | P(1)−C(13) | 1.830(2) | P(1)−C(13) | 1.817(3) |
| N(2)−C(1) | 1.341(4) | N(1)−C(25) | 1.364(4) | C(13)−C(18) | 1.411(3) | C(13)−C(18) | 1.421(4) |
| C(1)−C(5) | 1.384(5) | C(25)−C(24) | 1.419(4) | | | N(1)−Li | 1.985(5) |
| | | N(1)−Li(1) | 2.043(6) | | | P(1)−Li | 2.618(3) |
| | | N(2)−Li(1) | 2.012(7) | | | O(1)−Li | 1.963(4) |
| | | O(1)−Li(1) | 1.949(6) | | | O(2)−Li | 1.901(4) |
| | | O(2)−Li(1) | 1.939(6) | | | | |
| | | | | C(7)−P(1)−C(1) | 102.63(12) | C(7)−P(1)−C(1) | 104.02(14) |
| N(1)−P(1)−C(6) | 104.09(16) | N(2)−P(1)−C(1) | 104.24(14) | C(7)−P(1)−C(13) | 102.18(11) | C(7)−P(1)−C(13) | 103.90(13) |
| N(1)−P(1)−C(12) | 100.01(14) | N(2)−P(1)−C(7) | 100.29(15) | C(1)−P(1)−C(13) | 100.07(11) | C(1)−P(1)−C(13) | 101.84(12) |
| C(6)−P(1)−C(12) | 101.76(15) | C(1)−P(1)−C(7) | 97.10(13) | N(1)−P(2)−C(19) | 100.65(11) | N(1)−P(2)−C(19) | 106.86(12) |
| C(1)−N(1)−P(1) | 124.7(2) | C(25)−N(2)−P(1) | 118.9(2) | N(1)−P(2)−C(25) | 102.92(10) | N(1)−P(2)−C(25) | 100.36(12) |
| P(1)−N(1)−H(1) | 117.6 (3) | | | C(19)−P(2)−C(25) | 100.92(12) | C(19)−P(2)−C(25) | 100.40(12) |
| C(1)−N(2)−C(2) | 117.1(3) | C(25)−N(1)−C(21) | 118.5(3) | C(18)−N(1)−P(2) | 125.88(17) | C(18)−N(1)−P(2) | 116.45(18) |
| N(2)−C(1)−N(1) | 115.1(3) | N(1)−C(25)−N(2) | 113.3(3) | P(1)−C(13)−C(18) | 117.83(18) | P(1)−C(13)−C(18) | 115.30(18) |
| | | C(21)−N(1)−Li(1) | 152.7(3) | N(1)−C(18)−C(13) | 120.0(2) | N(1)−C(18)−C(13) | 118.4(2) |
| | | C(25)−N(1)−Li(1) | 88.4(3) | | | C(13)−P(1)−Li | 88.99(12) |
| | | C(25)−N(2)−Li(1) | 89.9(3) | | | C(7)−P(1)−Li | 110.91(12) |
| | | P(1)−N(2)−Li(1) | 148.7(2) | | | C(1)−P(1)−Li | 139.66(14) |
| | | | | | | C(18)−N(1)−Li | 114.99(19) |
| | | | | | | P(2)−N(1)−Li | 126.34(14) |
| | | | | | | N(1)−Li−P(1) | 76.31(11) |
| | | N(1)−Li(1)−N(2) | 68.1(2) | | | N(1)−Li−O(2) | 129.3(2) |
| | | N(2)−Li(1)−O(1) | 118.0(3) | | | N(1)−Li−O(1) | 120.2(2) |
| | | N(2)−Li(1)−O(2) | 117.5(3) | | | O(1)−Li−O(2) | 100.31(18) |
| | | O(1)−Li(1)−O(2) | 111.0(3) | | | P(1)−Li−O(1) | 102.93(15) |
| | | O(2)−Li(1)−N(1) | 113.2(3) | | | P(1)−Li−O(2) | 125.4(2) |
| | | O(1)−Li(1)−N(1) | 123.3(3) | | | | |

in a tetrahydrofuran solution [Equation (2)]. Complex **2** is bright yellow and is highly soluble in organic solutions. By cooling to −78 °C a crystallized product was obtained and subsequently characterized by low-temperature X-ray diffraction (Figure 3, Table 1) and spectroscopic methods.



**2**

(2)

X-ray analysis shows that the complex has a structure containing one symmetrical diazaallyl moiety as the core unit [Li(1)−N(1)−C(25)−N(2)] bonded in addition to two equidistant molecules of tetrahydrofuran, forming a tetracoordinated lithium atom.

Comparison of the neutral and the lithiated complex indicates the electronic effects introduced by the lithium atom. In the neutral compound the aromatic carbon atom exhibits a shorter distance to the pyridine nitrogen atom [N(2)−C(1) = 1.341(4) Å] than to the aminophosphane nitrogen atom [N(1)−C(1) = 1.391(4) Å]. In the lithiated complex the distances become almost equivalent [N(1)−C(25) = 1.364(4) Å and N(2)−C(25) = 1.355(4) Å] and are very close to the geometrical average in the neutral compound. The N(1)−C(25) and C(25)−C(24) bonds [1.418(4) Å] are longer than those in the neutral compound, for which N(2)−C(1) and C(1)−C(5) = 1.384(5) Å, respec-

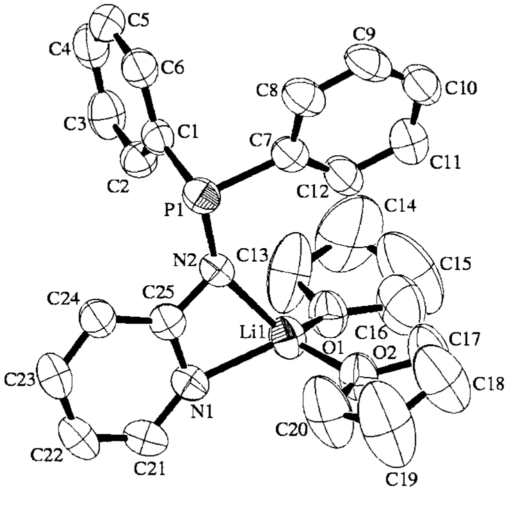


Figure 3. Molecular structure of complex **2**; thermal ellipsoids given at 50% probability

tively. The charge has little effect on the N−P bond length as N(2)−P(1) = 1.676(3) Å and N(1)−P(1) = 1.695(3) Å for **2** and **1**, respectively.

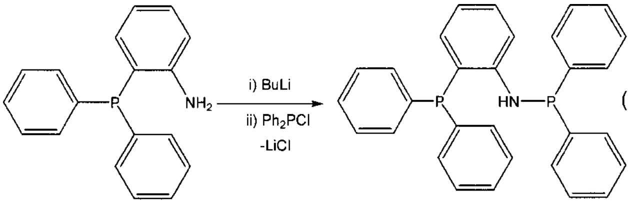
The Li−N(Py) bond length in complex **2** [2.043(6) Å] lies in the middle of the range (1.96−2.19 Å) indicated by other well-defined lithium complexes bearing a pyridine ring (Table 2).

Table 2. Li−N(Py) bond lengths in representative complexes

| Complex | Li−N(Py) [Å] | Ref. |
|---|---|---|
| [(THF)$_2$Li(2-Py)$_2$CH] | 1.966(4), 1.973(4) | [24] |
| [{(2-Py)NP(μ-N*t*Bu}Li$_2$·{Li(*t*BuN)$_2$P}] | 2.002(6) | [11d] |
| [Li$_8$(C$_5$H$_3$NMeNH)$_6$(O)(OEt$_2$)$_2$] | 2.01(1), 2.01(1) | [11a] |
| [Li(Py)$_2$(PNSiMe$_3$)]$_2$ | 2.028(3), 2.038(3) | [25] |
| {[Li(A-PySiMe$_3$)](THF)}$_2$[a] | 2.042(7) | [11b] |
| [Li(PyNPPh$_2$)$_2$(THF)$_2$] (**2**) | 2.043(6) | this paper |
| [MeSi(2-Py)$_3$LiX] (X = Br$_{0.2}$Cl$_{0.8}$) | 2.051(5), 2.081(4) | [26] |
| [{*t*BuNP(μ-N*t*Bu)$_2$PN(2-Py)}Li$_2$] | 2.093(3) | [11b] |
| [Li(bpg)(H$_2$O)]·H$_2$O[b] | 2.152(3), 2.187(3) | [27] |

[a] A-PySiMe$_3$ = 6-methyl-2-(trimethylsilylamino)pyridine. [b] bpg = *N*,*N*-bis(2-pyridylmethyl)glycine.

The organic compound *N*,2-bis(diphenylphosphanyl)benzenamine (**3**) was prepared from deprotonated 2-(diphenylphosphanyl)benzeneamine with butyllithium and concomitant addition of chlorodiphenylphosphane [Equation (3)].[14] Pale yellow single crystals of **3** suitable for X-ray diffraction (Figure 4, Table 1) were obtained by recrystallization from toluene at −40 °C.



(3)

**3**

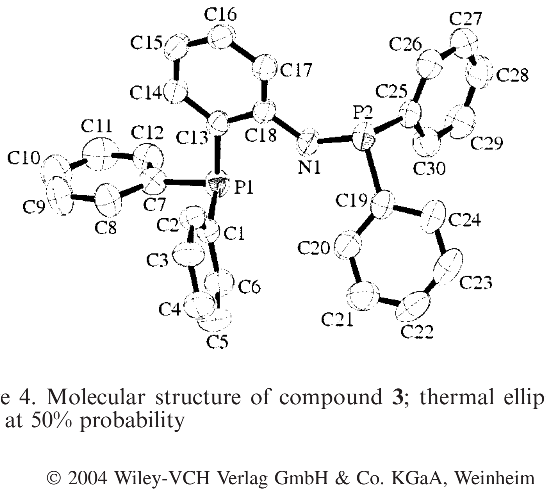
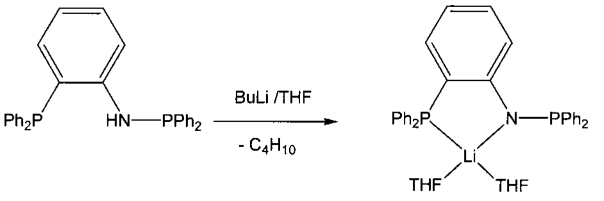


Figure 4. Molecular structure of compound **3**; thermal ellipsoids given at 50% probability

The corresponding lithium *N*,2-bis(diphenylphosphanyl)benzenamine (**4**) was prepared by deprotonation of *N*,2-bis(diphenylphosphanyl)benzenamine (**3**) with butyllithium [Equation (4)]. The reaction proceeds in THF in good yield (85%), producing a yellow product that can be easily recrystallized from THF at −20 °C.



(4)

**4**

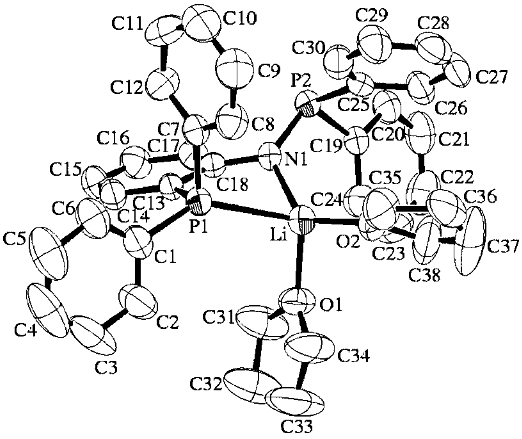
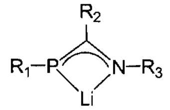
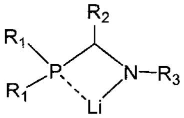
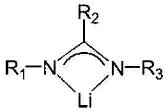
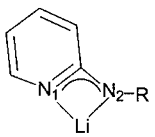
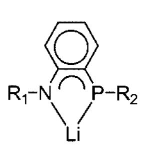


Figure 5. Molecular structure of complex **4**; thermal ellipsoids given at 50% probability

The X-ray structure of complex **4** (Figure 5, Table 1) shows a core unit of a five-membered ring, P(1)−C(13)−C(18)−N(1)−Li, with the lithium atom tilted down from the plane formed by the four additional atoms. The lithium atom is coordinated by the nitrogen atom and *ortho*-phosphorus atom in addition to two molecules of THF, forming a highly distorted tetrahedron. Whereas the average Li−O bond length in lithiated complexes is normally around 1.92−1.94 Å, in complex **4** one bond is rather short and the second is rather long [O(2)−Li = 1.901(4) Å and O(1)−Li = 1.963(4) Å]. This increase is a result of the rejection of the lone pair of electrons of one oxygen atom and one of the phosphorus atoms [O(1)−P(1) = 3.61 Å]. Interestingly, no interaction is exhibited between the lithium atom and the phosphorus atom attached to the nitrogen atom. Seemingly, this interaction induces a higher energy and is observed only when no other donating atoms are present in sterically less demanding positions.[28] Comparison of the neutral and lithiated complexes shows that the increase in charge at the nitrogen atom causes almost no change in aromatic C−C bond lengths, although the bonds connecting the substituents to the aromatic ring do lengthen, i.e. C(13)−C(18) = 1.421(4) Å, N(1)−C(18) =

Table 3. Comparison of bond angles and lengths in four- and five-membered ring *N*,*N*- and *N*,*P*-ligated lithium complexes

| | Complex | Bond angles [°]<br>Bond lengths [Å] | Ref. |
|---|---|---|---|
| Four-membered ring complexes: | | | |
|  | [Li{P(Ph)C(Ph)NSiMe$_2$tBu}(THF)]$_2$ | N–Li–P = 68.0(3)<br>Li–N = 1.991(10)<br>Li–P = 2.641(9) | [15] |
|  | [Ph$_2$PC{NiPr}$_2$Li(TMEDA)] | N–Li–P = 66.54(16)<br>Li–N = 1.927(5)<br>Li–P = 2.625(5) | [29] |
|  | [Li(FIso)(THF)$_2$][a] | N(1)–Li–N(2) = 68.2(1)<br>Li–N(1) = 2.036(4)<br>Li–N(2) = 2.041(4) | [9a] |
| | [PhC(NSiMe$_3$)$_2$Li(TMEDA)] | N(1)–Li–N(2) = 69.19(19)<br>Li–N(1) = 2.019(6)<br>Li–N(2) = 2.033(6) | [19] |
|  | {[Li(A-PySiMe$_3$)](thf)}$_2$[b] | N(1)–Li–N(2) = 67.4(2)<br>Li–N(1) = 2.042(7)<br>Li–N(2) = 2.097(7) | [11b] |
| | [Li(PyNPPh$_2$)$_2$(thf)$_2$] (**2**) | N(1)–Li–N(2) = 68.1(2)<br>Li–N(1) = 2.043(6)<br>Li–N(2) = 2.012(7) | this work |
| Five-membered ring coplexes: | | | |
|  | [Ph$_2$PC$_6$H$_4${2-N(2,6-Me$_2$Ph)}Li(thf)$_2$] | N–Li–P = 76.63(17)<br>Li–N = 1.990(5)<br>Li–P = 2.620(5) | [16a] |
| | [Ph$_2$PC$_6$H$_4${2-N(C$_6$H$_4$PPh$_2$)}Li(thf)$_2$] | N–Li–P = 73.09(15), 73.35(15)<br>Li–N = 2.039(5)<br>Li–P = 2.779(5), 2.824(5) | [16b] |
| | [PPh$_2$PC$_6$H$_4$(2-NPPh$_2$)Li(thf)$_2$] (**4**) | N–Li–P = 76.31(11)<br>Li–N = 1.985(5)<br>Li–P = 2.618(3) | this work |

[a] Fiso = *N*,*N*-bis(2,6-diisopropylphenyl)formamidine. [b] A-PySiMe$_3$ = 6-methyl-2-(trimethylsilylamino)pyridine.

1.386(3) Å, P(1)−C(13) = 1.817(3) Å, and C(14)−C(19) = 1.411(3) Å, N(1)−C(18) = 1.402(3) Å, P(1)−C(13) = 1.830(3) Å, for **4** and **3**, respectively. Notably, the distance between the *ortho* substituents decreases only slightly upon the attachment of the lithium atom: N(1)−P(1) = 2.99 and 2.80 Å in **3** and **4**, respectively.

Comparison of the Li−N bond lengths in complexes **2** and **4** is of interest. In complex **2** the average bond length of 2.02 Å is a result of resonance among the aminopyridine ring whereas in complex **4** a shorter bond length [1.985(6) Å] is observed. This difference in bonding also occurs in other lithium benzamidinate complexes.[9]

The rings formed by the metal atom and the *N*,*P*- and *N*,*N*-ancillary ligations are also of interest. When four-membered rings are formed, the N−Li−P or N−Li−N bond angle is within 66.5−69.2°, while for five-membered rings this angle is between 73.0 and 76.6° (Table 3). The N−Li−N angle in the four-membered ring in complex **2** is similar to that found in benzamidinate complexes, whereas the N−Li−P angle in the five-membered ring in complex **4** exhibits an angle close to the highest observed value (76.31°).

## Conclusions

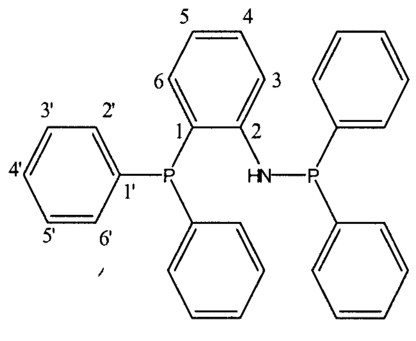
Two lithium complexes and their corresponding parent neutral ligands have been characterized by single-crystal X-ray diffraction. In the phosphanylpyridine complex **2** the metal ion is coordinated to the hard nitrogen ligands, forming a constrained four-membered metallacycle, regardless of possible coordination with the soft phosphorus atom to form a less constrained five-membered ring. In the diphosphane complex **4** the metal ion forms a five-membered ring that connects soft and hard moieties. Coordination to the second phosphorus moiety is sterically hindered.

## Experimental Section

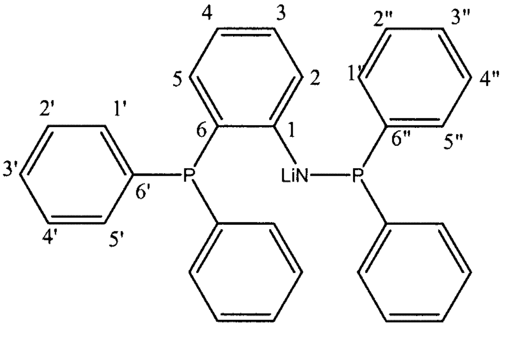
**General Remarks:** All manipulations of air-sensitive materials were carried out with the vigorous exclusion of oxygen and moisture in flame dried Schlenk-type glassware connected to a dual-manifold Schlenk line, or interfaced to a high-vacuum ($10^{-6}$ Torr) line, or in a nitrogen-filled Vacuum Atmospheres glove box with a medium-capacity recirculator (1−2 ppm $O_2$). Argon and nitrogen were purified by passage through an MnO oxygen-removal column and a Davison molecular sieves (4-Å) column. THF and [$D_8$]THF solvents were distilled under argon from sodium/benzophenone. Hydrocarbon solvents ($C_6D_6$, toluene) were distilled under nitrogen from Na/K alloy. All solvents for vacuum-line manipulations were stored in vacuo over Na/K alloy in resealable bulbs. The neutral ligands $Ph_2PNPy$ (**1**) (Py = pyridine) and *ortho*-$Ph_2PNHC_6H_4PPh_2$ (**3**) were prepared according to literature methods.[23] NMR spectra were recorded with Bruker Avance 300 and 500 spectrometers. Chemical shifts for $^1H$ and $^{13}C$ NMR are referenced to internal solvent resonance and are reported relative to tetramethylsilane. Experiments were conducted in Schlenk vessel sealed tubes (J. Young stopcock) after vacuum transfer of the solvent in a high-vacuum line.

**Synthesis of Li($Ph_2PNPy$)($THF)_2$ (2):** *n*BuLi (0.24 g, 3.78 mmol as a 1.6 M solution in hexane) was added dropwise at −78 °C under nitrogen to a stirred solution of the ligand $Ph_2PNHPy$ (1.05 g, 3.78 mmol) in THF (20 mL). After stirring at −78 °C for 30 min, the resultant solution was allowed to warm to room temperature and stirred for a further 12 h. After the resulting solution was concentrated to 3 mL and cooled slowly to −78 °C, yellow crystals precipitated; 1.45 g (95%). $C_{25}H_{30}LiN_2O_2P$ (428.4 g): calcd. C 70.09, H 7.06, N 6.54; found C 69.69, H 7.40, N 6.27. $^1H$ NMR ($C_4D_8O$, 300 MHz): $\delta$ = 1.73 (m, 4 H, $\mathrm{C}\mathit{H}_2\mathrm{CH_2O}$), 3.57 (m, 4 H, $\mathrm{C}\mathit{H}_2\mathrm{O}$), 6.05 (dd, $^3J$ = 5.1 Hz; $^3J$ = 6.3 Hz, 1 H, NCHC*H*CHCHC), 6.56 (d, $^3J$ = 8.1 Hz, 1 H, NCHCHCHC*H*C), 7.12 (dd, $^3J$ = 6.3, $^3J$ = 8.1 Hz, 1 H, NCHCHC*H*CHC), 7.15 (m, 6 H, 2 × $C_6H_5$ *m*- and *p*-H), 7.32 (m, 4 H, 2 × $C_6H_5$ *o*-H), 7.63 (d, $^3J$ = 5.1 Hz, 1 H, NC*H*CHCHCHC) ppm. $^{13}C$ NMR ($C_4D_8O$, 150 MHz): $\delta$ = 22.5, 64.1, 105.3, 107.2 (d, $^1J_{\text{c-p}}$ = 30.0 Hz), 124.5, 124.9, 125.0, 128.5, 128.7, 133.9 (d, $^3J_{\text{c-p}}$ = 7.5 Hz), 144.4 ppm. $^{31}P$ NMR ($C_6D_6$): $\delta$ = 32.14 ppm.

**Synthesis of $Ph_2PNHC_6H_4PPh_2$ (3):** $Ph_2PNHC_6H_4PPh_2$ was synthesized according to a reported method.[12] This procedure involves the deprotonation of 2-(diphenylphosphanyl)benzeneamine with BuLi, followed by reaction with $PPh_2Cl$ to obtain the product.[12] Single crystals for X-ray diffraction were obtained by recrystallization from toluene at −40 °C. $^1H$ NMR ($C_6D_6$, 300 MHz): $\delta$ = 5.88 (m, 1 H, $C_6H_4$ 3-H), 6.68 (m, 1 H, $C_6H_4$ 5-H), 6.96 (m, 1 H, $C_6H_4$ 6-H), 7.03−7.19 (m, 14 H, $C_6H_5$ 2′-,6′′-H and non-marked rings), 7.30−7.41 (m, 6 H, $C_6H_5$ 3′-,5′-H), 7.72 (m, 1 H, $C_6H_4$ 4-H) ppm. $^{13}C$ NMR ($C_6D_6$, 150 MHz): $\delta$ = 115.5, 116.0, 120.4, 127.8, 128.3, 128.8, 129.0, 129.1, 129.29, 129.35, 131.5, 131.9, 134.3, 134.6, 135.1, 135.2, 150.5 ppm. $^{31}P$ NMR ($C_6D_6$): $\delta$ = 21.01 ($P_A$), 28.01 ($P_X$) ppm.



**Synthesis of Li($Ph_2PNC_6H_4PPh_2$)($THF)_2$ (4):** *n*BuLi (0.347 g, 5.42 mmol, 1.6 M solution in hexane) was added dropwise at −78 °C under nitrogen to a stirred solution of the ligand $Ph_2PNHC_6H_4PPh_2$ (2.50 g, 5.42 mmol) in THF (50 mL). After stirring at −78 °C for 30 min, the obtained solution was allowed to warm to room temperature and stirred for a further 12 h. The resulting solution was then concentrated to dryness to obtain 2.15 g (85%) of yellow product. Single crystals for X-ray diffraction were obtained by recrystallization of the solid from THF at −20 °C. $C_{38}H_{40}LiNP_2O_2$ (611.2 g): calcd. C 74.61, H 6.60, N 2.29; found C 72.71, H 6.61, N 2.59. $^1H$ NMR ($C_4D_8O$, 300 MHz): $\delta$ = 1.76 (m, 4 H, $CH_2CH_2O$), 3.62 (m, 4 H, $CH_2O$), 6.09 (m, 1 H, $C_6H_4$ 3-H), 6.37 (m, 1 H, $C_6H_4$ 5-H), 6.78 (m, 1 H, $C_6H_4$ 6-H), 6.91−7.02 (m, 6 H, $C_6H_5$ 1′-,3′-,5′-H), 7.18−7.22 (m, 6 H, $C_6H_5$ 1′′-,3′′-,5′′-H), 7.23−7.28 (m, 8 H, $C_6H_4$ 2′-,2′′-,4′-,4′′-H), 7.34 (m, 1 H, $C_6H_4$ 4-H) ppm. $^{13}C$ NMR ($C_4D_8O$, 150 MHz): $\delta$ = 26.5, 68.6, 114.5 (d, $^1J_{\text{c-p}}$ = 30.0 Hz), 119.6, 120.2, 120.3, 128.1, 129.1, 129.2, 130.0, 130.08, 130.16, 131.9, 131.9, 133.2, 133.6, 134.8, 134.8, 135.7, 136.0, 140.1, 149.6 (d, $^2J_{\text{c-p}}$ = 20.0 Hz) ppm. $^{31}P$ NMR: ($C_6D_6$): $\delta$ = 12.99 ($P_A$), 42.46 ($P_X$) ppm.



**X-ray Crystallographic Study:** X-ray crystallographic experiments were carried out with a Nonius Kappa CCD diffractometer with graphite-monochromatized Mo-$K_\alpha$ radiation ($\lambda$ = 0.71073 Å). Crystals were placed in a Parothone N oil in a glove box. Single crystals were mounted on the diffractometer under a stream of cold $N_2$ at 230 K. Data were collected using $\omega$ and $\varphi$ scans to cover the Ewald sphere. Accurate cell parameters were obtained with refined collections of intensities and were corrected in the usual way. Structures were solved by direct methods and completed using successive Fourier difference maps. Refinements were performed anisotropically with respect to the non-hydrogen atoms. Hydrogen atoms were placed at calculated positions and refined using the riding model until convergence was reached. Data collection and reduction, cell refinements were carried out with the Nonius software package.[30] Structure solution and refinement were carried out by the SHELXS-97[31] and SHELXL-97[32] software packages, respectively. The ORTEP program incorporated in the TEXRAY Structure Analysis Package was used for molecular graphics.[33] Details are listed in Table 4. CCDC-250098 to -250101 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: + 44-1223-336-033; E-mail: deposit@ccdc.cam.ac.uk].

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Table 4. Crystal data collection for complexes **1**−**4**

| | **1** | **2** | **3** | **4** |
|---|---|---|---|---|
| Empirical formula | $C_{17}H_{15}N_2P$ | $C_{25}H_{30}OLiN_2O_2P$ | $C_{30}H_{25}NP_2$ | $C_{38}H_{40}LiNO_2P_2$ |
| Formula mass | 278.28 | 428.42 | 461.45 | 611.59 |
| Temperature [K] | 230.0(1) | 230.0(2) | 230.0(1) | 230.0(2) |
| Wavelength [Å] | 0.71070 | 0.71070 | 0.71070 | 0.71070 |
| Crystal system, space group | monoclinic, *C*2/*c* | monoclinic, *P*21/*n* | triclinic, $P\bar{1}$ | monoclinic, *P*21/*n* |
| Unit cell dimensions: | | | | |
| *a* [Å] | 27.0230(15) | 10.1860(3) | 10.4130(8) | 11.2180(3) |
| *b* [Å] | 8.2640(6) | 14.4800(5) | 10.5580(11) | 17.0050(6) |
| *c* [Å] | 14.2330(11) | 16.2270(7) | 12.1650(11) | 18.7330(6) |
| $\alpha$ [°] | 90 | 90 | 77.967(6) | 90 |
| $\beta$ [°] | 114.444(3) | 95.5900(16) | 75.626(6) | 106.1630(19) |
| $\gamma$ [°] | 90 | 90 | 75.058(4) | 90 |
| $V$ [Å$^3$] | 2893.6(3) | 2381.99(15) | 1236.8(2) | 3432.30(19) |
| $Z$ | 8 | 4 | 2 | 4 |
| $D_{\text{calcd.}}$ [g/cm$^3$] | 1.278 | 1.195 | 1.239 | 1.184 |
| $\mu$ [mm$^{-1}$] | 0.181 | 0.138 | 0.194 | 0.160 |
| *F*(000) | 1168 | 912 | 484 | 1296 |
| Crystal size [mm] | 0.15 × 0.10 × 0.10 | 0.30 × 0.18 × 0.09 | 0.25 × 0.33 × 0.42 | 0.30 × 0.21 × 0.15 |
| $\theta$ range for data collection [°] | 2.60−25.05 | 2.27−25.04 | 1.75−25.05 | 1.65−25.02 |
| Limiting indices: | | | | |
| *h* | $0 \le h \le 32$ | $-12 \le h \le 12$ | $0 \le h \le 12$ | $0 \le h \le 13$ |
| *k* | $0 \le k \le 9$ | $17 \le k \le 16$ | $-11 \le k \le 12$ | $0 \le k \le 20$ |
| *l* | $-16 \le l \le 15$ | $9 \le l \le 19$ | $-13 \le l \le 14$ | $-22 \le l \le 21$ |
| Reflections collected/unique | 2561/2561 [*R*(int) = 0.0000] | 7201/4159 [*R*(int) = 0.0461] | 4381/4381 [*R*(int) = 0.0000] | 6043/6043 [*R*(int) = 0.0000] |
| Completeness to $\theta = 25.05°$ | 99.7% | 98.8% | 99.8% | 99.7% |
| Max./min. transmission | 0.9821/0.9734 | 0.9877/0.9597 | 0.9857/0.9689 | 0.9765/0.9537 |
| Refinement method | full-matrix least squares on $F^2$ | full-matrix least squares on $F^2$ | full-matrix least squares on $F^2$ | full-matrix least squares on $F^2$ |
| Data/restraints/parameters | 2561/0/196 | 4159/0/302 | 4381/0/323 | 6043/0/506 |
| Goodness-of-fit on $F^2$ | 1.065 | 0.916 | 1.027 | 1.046 |
| Final *R* indices [$I > 2\sigma(I)$] | $R1 = 0.0676$,<br>$wR2 = 0.1450$ | $R1 = 0.0594$,<br>$wR2 = 0.1583$ | $R1 = 0.0486$,<br>$wR2 = 0.1133$ | $R1 = 0.0547$,<br>$wR2 = 0.1257$ |
| *R* indices (all data) | $R1 = 0.1159$,<br>$wR2 = 0.1650$ | $R1 = 0.1242$,<br>$wR2 = 0.1728$ | $R1 = 0.0934$,<br>$wR2 = 0.1240$ | $R1 = 0.1022$,<br>$wR2 = 0.1405$ |
| Largest difference peak/hole [e·A$^{-3}$] | 0.295/−0.331 | 0.460/−0.412 | 0.176/−0.234 | 0.312/−0.246 |

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