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Coordination Behavior of the (Diphenylphosphanyl)[α-(2-pyridyl)benzyl]amide Anion toward Lithium and Zinc Cations

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A two-step synthesis allows the preparation of [α-(2-pyridyl)-benzyl]amine (**1**) in good yield. Phosphanylation in the presence of triethylamine gives (diphenylphosphanyl)[α-(2-pyridyl)benzyl]amine (**2**), which crystallizes as a racemate in the centrosymmetric triclinic space group $P\bar{1}$. The P–N bond lengths exhibit an average value of 168.3 pm. Lithiation of **2** with *n*-butyllithium yields dimeric semi(tetrahydrofuran)lithium (diphenylphosphanyl)[α-(2-pyridyl)benzyl]amide (**3**) with the lithium atoms in different environments. One Li atom is in a distorted tetrahedral environment and the other in a trigonal-planar coordination sphere with bridging amide moieties (av. Li–N 201.8, Li–O 192.4 pm). Zincation of **2** with dimethylzinc leads to the formation of dimeric methylzinc (diphenylphosphanyl)[α-(2-pyridyl)benzyl]amide (**4**) with a central six-membered $(ZnNP)_2$ ring in a boat conformation (av. Zn–N 201.8, Zn–P 245.9 pm). The endocyclic P–N bonds are rather short (av. value 162.7 pm).

Introduction

Primary and secondary (2-pyridylmethyl)amines (H_2L) offer a surprisingly wide spectrum of reactivity depending on the *N*-substituent. Deprotonation with organometallics such as LiR and ZnR_2 leads to the formation of the corresponding lithium and zinc amides.[1–8] Starting from these amides $(HL)^-$ (Scheme 1) a fascinating chemistry opens up. A second metalation step yields the dianion $(L)^{2-}$, which is stabilized by delocalization of the negative charge and behaves mostly as a bis(amide).[2,5] These bis(amides) can be oxidized, thereby leading to radical anions $(L^{ox1})^{\cdot-}$, which easily dimerize with C–C bond formation to $(L^{ox1}{}_2)^{2-}$.[1–3,9] Another single-electron oxidation yields the neutral imines $(L^{ox2})^0$. The reaction behavior of the secondary (2-pyridylmethyl)amines strongly depends on the metalating power of the organometallics, the redox potential of the metals, and also on the nature of the *N*-bound group R, the bulkiness and electronic properties of which play a key role. If R represents a *tert*-butyl group, an equilibrium between the radical anion $(L^{ox1})^{\cdot-}$ and its dimer $(L^{ox1}{}_2)^{2-}$ was observed in solution,[10–13] whereas in the solid state only the dimer was found.[13,14] If trialkylsilyl groups are bound at the amide nitrogen atom, the radical anion $(L^{ox1})^{\cdot-}$ was neither detected in solution nor in the solid state.[1,2] However, the metathesis reaction of $Na(L^{ox1})$ with $ZnCl_2$ allowed the isolation of crystalline $Zn(L^{ox1})_2$ when bulky aryl groups were bound at the amido group.[15]

The redox potential of the organometallics determines whether an oxidative C–C coupling reaction occurs. Organolithium and -magnesium reagents are able to doubly deprotonate (2-pyridylmethyl)amines to give $(L)^{2-}$, but the redox potentials of these metals prevent an oxidative C–C coupling reaction.[2,5] Oxidation can be achieved by addition of an oxidizing reagent. Thus, addition of white phosphorus to a solution of $Li_2(L)$ leads to the formation of $Li_2(L^{ox1}{}_2)$ and Li_3P_7.[9] Dialkylzinc is a weaker metalating reagent, and higher temperatures are necessary to perform a double deprotonation. However, under these reaction conditions the dianion is immediately oxidized, and zinc metal precipitates from the reaction mixture, thus yielding the dinuclear zinc complex of $(L^{ox1}{}_2)^{2-}$, namely, $(RZn)_2(L^{ox1}{}_2)$.[1,2] Even stronger oxidizing reagents such as iron(III) compounds are necessary to prepare the imines $(L^{ox2})^0$ by means of a second oxidation step.[16] It is noteworthy that the oxidative C–C coupling reaction occurs only with deprotonated (2-pyridylmethyl)amines, whereas (2-pyridylmethyl)amine (H_2L) itself can act as a ligand even for iron(III) if deprotonation is impossible due to a lack of nucleophilicity of the anion [see, for example, the (H_2L) complexes of iron chlorides].[17] Also, adducts of (2-pyridylmethyl)amine with zinc(II) are well known without deprotonation reactions if anions without nucleophilic character are present {see, for example, the complexes of zinc(II) halide of the types $[(H_2L)ZnX_2]$, $[(H_2L)_2ZnX_2]$, and $[(H_2L)_3ZnX_2]$}.[18]

The influence of another Lewis base at the amide nitrogen atom was investigated by using (diphenylphosphanyl)(2-pyridylmethyl)amine.[19] The *N*-bound diphenylphosphanyl group allows the detection of the reaction by means of $^{31}P\{^1H\}$ NMR spectroscopy; however, it also influences the chemistry of the (2-pyridylmethyl)amines. On

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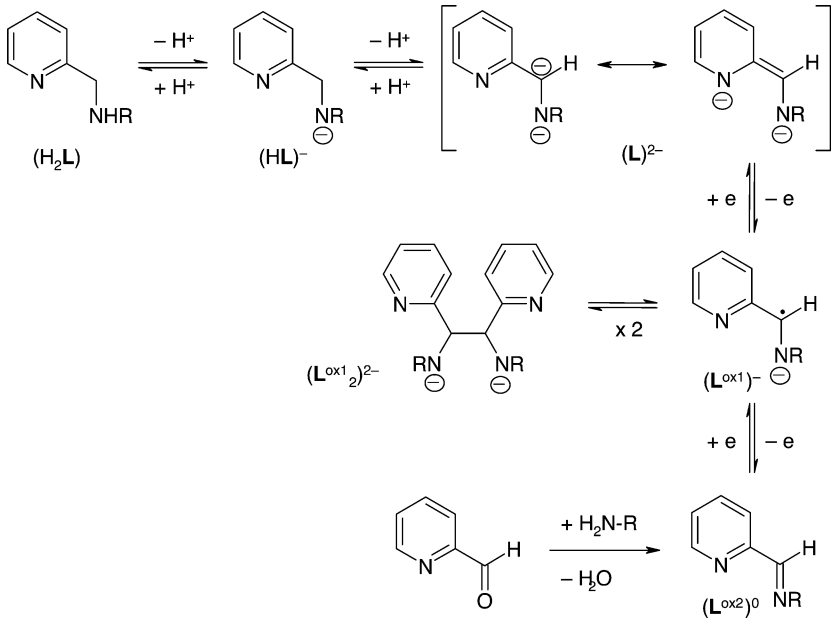
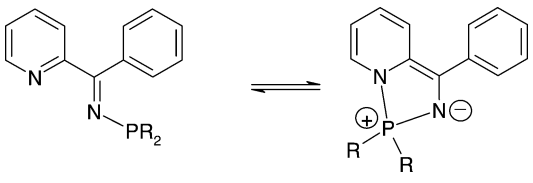


Scheme 1. Reactivity pattern of (2-pyridylmethyl)amines. The upper line shows the deprotonation/protonation equilibria, the right column the oxidation/reduction equilibria.

the one hand, another coordination site at the phosphorus moiety is available; on the other hand, the oxidative C–C coupling reaction is hindered in comparison to compounds with *N*-bound trialkylsilyl groups.[19]

Several experiments showed that delocalization of the anionic charge represents a requirement for the oxidation of these amines. Therefore, [2-(2-pyridyl)ethyl]amine can only be deprotonated once, and no C–C coupling occurs under similar reaction conditions.[20] Other preparative procedures are necessary to synthesize 1,4-diamino-2,3-bis(2-pyridyl)-butanes.[21] We were interested in the influence of a phenyl group at the methylene moiety of the (2-pyridylmethyl)-amines on the coordination behavior of ligand $(HL)^-$. Due to the fact that a phenyl group raises the acidity of the remaining proton and would be able to interfere with the charge after a second deprotonation, the diphenylphosphanyl group was chosen to suppress a second deprotonation step, thus avoiding the formation of (phosphanyl)[α-(2-pyridyl)benzylidene]amines. Dyer et al.[22] already showed that these compounds act as N,P-chelating ligands for rhodium(II), palladium(II), and platinum(II) and that these complexes are able to copolymerize carbon monoxide and alkene. In addition, an equilibrium according to Equation (1) was observed depending on the *P*-bound substituents. With R = Ph the monocyclic "open" form is favored,[22] whereas the bicyclic "closed" form with the broken aromaticity is the major component for R = N*i*Pr$_2$.[23]

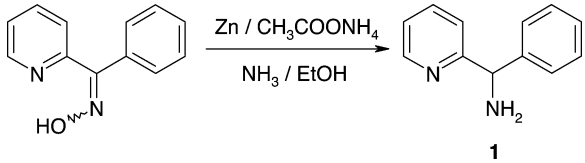


(1)

Results and Discussion

Synthesis of [α-(2-Pyridyl)benzyl]amine (1)

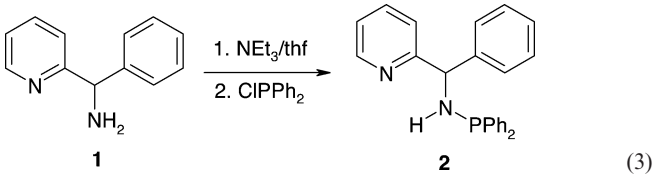
The synthesis of **1** was accomplished by means of a two-step procedure starting from commercially available phenyl 2-pyridyl ketone according to a literature procedure.[24] A subsequent reduction of the oxime in a heterogenic mixture of zinc, ammonium acetate, and ammonia in ethanol yielded racemic **1** as a light yellow oil after distillation in vacuo according to Equation (2).[25] Our present investigations focus on the coordination chemistry of these bidentate bases, and therefore (*S*) and (*R*) enantiomers of **1** were not separated.



1 (2)

The introduction of *N*-phosphanyl substituents[19] at the amide functionality of (2-pyridylmethyl)amine is possible through a two-step sequence that involves lithiation of the amine at –78 °C followed by a metathesis reaction with chlorodiphenylphosphane to yield (diphenylphosphanyl)(2-pyridylmethyl)amine. The additional phenyl group at the methylene unit did not hinder this reaction sequence, but we also obtained at least two minor byproducts, namely, bis(diphenylphosphanyl)[α-(2-pyridyl)benzyl]amine and tetraphenyldiphosphane. Due to the fact that purification of (diphenylphosphanyl)[α-(2-pyridyl)benzyl]amine (**2**) through distillation or sublimation in vacuo failed, all reactions were accompanied by traces of these byproducts. To

suppress these side reactions, attempts were undertaken to employ milder deprotonation reagents. A mixture of triethylamine and catalytic amounts of 4-(dimethylamino)pyridine (dmap) was added to a solution of amine **1** in tetrahydrofuran. Whereas deprotonation and phosphanylation succeeded without formation of any byproduct, separation of the desired product **2** from an excess of dmap proved to be challenging. Therefore, we tested this reaction without the addition of catalytic amounts of dmap according to Equation (3). If an excess amount of NEt_3 (20 mol-%) was applied, product **2** was obtained in good yield after removal of solid triethylammonium chloride by filtration and excess triethylamine by distillation under reduced pressure.



1 **2** (3)

Figure 1 shows the molecular structure and numbering scheme of the (*S*) isomer of **2**. However, due to the centrosymmetric space group, the crystalline material contains a racemate of **2**. The hydrogen atom at N1 was refined freely, and the environment of the nitrogen atom N1 is nearly planar considering the estimated standard deviation (e.s.d.) values. The phosphorus atom P is embedded in a trigonal-pyramidal environment. The P–N1 bond of 168.3(2) pm is rather short, which can be understood as a consequence of a negative hyperconjugation from the p_z(N1) lone pair into a σ*(P–C19) orbital. This fact would also explain the slight elongation of the P–C19 bond [184.4(2) pm] relative to the P–C13 distance of 182.7(2) pm. Similar effects have been observed for bis(diphenylphosphanyl)(2-pyridylmethyl)-amine[19] as well as for *N*-trialkylsilyl-substituted (2-pyridylmethyl)amines.[26,27]

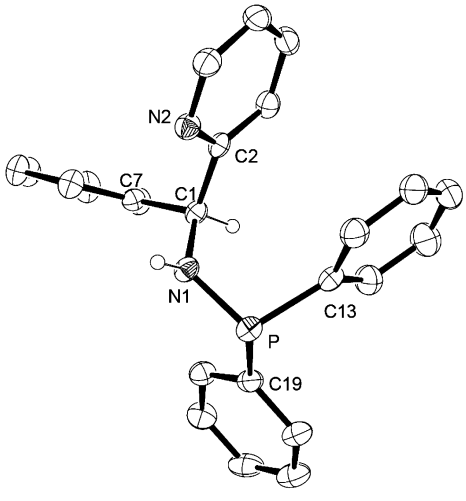
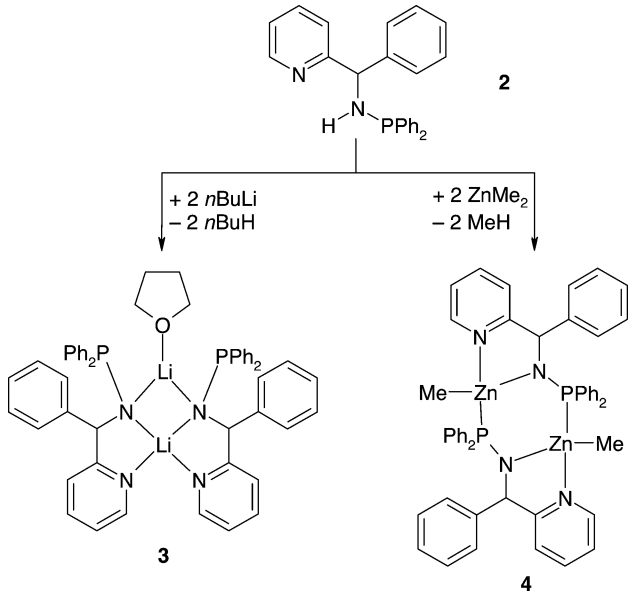


Figure 1. Molecular structure of the (*S*) isomer of **2**. The ellipsoids represent a probability of 40%. Aryl hydrogen atoms are omitted for clarity reasons. Selected bond lengths [pm] and angles [°]: P–N1 168.3(2), P–C13 182.7(2), P–C19 184.4(2), N1–C1 146.0(3), N1–H 83.0(2), C1–C2 152.4(3), C1–C7 152.5(3); C1–N1–P 124.64(15), C1–N1–H 115.0(16), P–N1–H 113.7(16), N1–P–C19 130.09(11), N1–P–C13 103.27(10), C19–P–C13 100.62(11).

Metalation of (Diphenylphosphanyl)[α-(2-pyridyl)-benzyl]amine (2)

Lithiation of **2** with *n*-butyllithium yielded colorless dimeric semi(tetrahydrofuran)lithium (diphenylphosphanyl)[α-(2-pyridyl)benzyl]amide (**3**) according to Scheme 2. In this dinuclear complex, the lithium atoms show different coordination environments. One lithium atom is surrounded tetrahedrally by four nitrogen atoms, whereas the other one is in a trigonal-planar environment of the two amide functionalities and an oxygen atom of the tetrahydrofuran molecule. A very similar molecular structure was observed for dimeric semi(tetrahydrofuran)lithium (*tert*-butyldimethylsilyl)(2-pyridylmethyl)amide.[5] Metalation of **2** with dimethylzinc gave heteroleptic complexes of colorless methylzinc (diphenylphosphanyl)[α-(2-pyridyl)-benzyl]amide (**4**), which crystallized from a solution in toluene as a dimer with tetracoordinate zinc atoms. In contrast to the lithium derivative, the zinc compound showed a different molecular structure from its trialkylsilyl congener, which formed a four-membered Zn_2N_2 ring.[1,2]



Scheme 2. Metalation of **2**.

Spectroscopic Characterization

Selected NMR spectroscopic data of **1**, **2**, **3**, and **4** are compared in Table 1. Due to the low solubility of **4** in hydrocarbons, the NMR spectroscopic data of this zinc compound were recorded as solutions in [D_8]thf. The resonances of the methine proton, of the tertiary carbon atom as well as of the ^{31}P atom, are shifted towards higher fields

upon phosphanylation and metalation due to an enhanced shielding of the nitrogen atom. Metalation also leads to significantly larger ^3J(H,P) coupling constants.

Table 1. Comparison of selected NMR spectroscopic data (chemical shifts, δ [ppm]; coupling constants, J [Hz]) of the unsubstituted amine **1** (in $CDCl_3$), the *N*-phosphanyl-substituted ligand **2** (in C_6D_6), the lithium salt **3** (in C_6D_6), and the methylzinc complex **4** (in [D_8]thf).

	1	**2**	**3**	**4**
^{1}H NMR				
$\delta(CH_{alkyl})$	5.17	5.48	5.76	5.46
^3J(H,P)	–	8.4	21.4	17.2
$^{13}C\{^1H\}$ NMR				
$\delta(CH_{alkyl})$	60.7	65.8	71.6	67.7
^2J(P,C)	–	22.4	13.7	20.8
$^{31}P\{^1H\}$ NMR				
δ(P)	–	42.2	52.4	46.8

Molecular Structures

The molecular structure of dimeric **3** is displayed in Figure 2. In principle, the three different (*S*,*S*), (*R*,*R*), and (*S*,*R*) isomers are possibly based on the chirality of the tertiary carbon atoms C6 and C30. This dimer nearly adopts C_2 symmetry and crystallizes in a centrosymmetric space group. Therefore, the crystalline material contains a racemate of the (*S*,*S*) and (*R*,*R*) isomers.

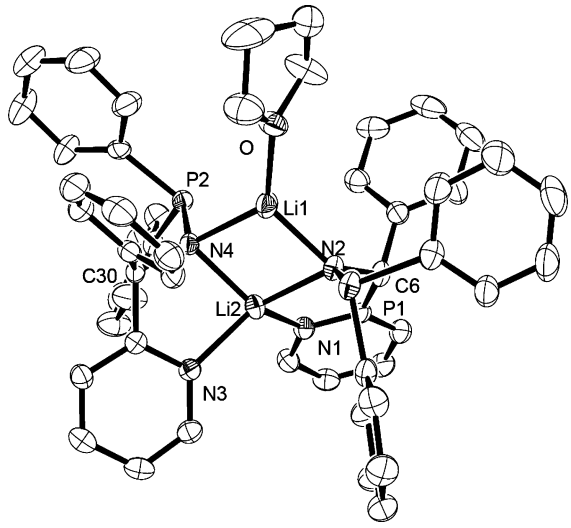


Figure 2. Molecular structure of dimeric **3**. The ellipsoids represent a probability of 40%. Hydrogen atoms are omitted for reasons of clarity. Selected bond lengths [pm] and angles [°]: Li1–O1 192.4(7), Li1–N2 200.1(6), Li1–N4 202.6(6), Li2–N1 199.8(6), Li2–N2 204.7(6), Li2–N3 204.3(6), Li2–N4 201.3(6), P1–N2 165.7(3), P2–N4 165.9(2), N2–C6 148.2(4), N4–C30 146.8(4); O–Li1–N2 127.2(3), O–Li1–N4 126.0(3), N2–Li1–N4 106.5(3), N1–Li2–N4 132.5(3), N1–Li2–N2 85.6(2), N4–Li2–N2 105.3(3), N1–Li2–N3 115.9(3), N4–Li2–N3 85.6(2), N2–Li2–N3 139.5(3), C6–N2–P1 120.1(2), C6–N2–Li1 132.5(3), P1–N2–Li1 99.0(2), C6–N2–Li2 109.5(3), P1–N2–Li2 113.2(2), C30–N4–P2 121.1(2), C30–N4–Li2 109.4(3), P2–N4–Li2 113.3(2), C30–N4–Li1 131.2(3), P2–N4–Li1 98.7(2), N2–P1–C19 110.15(16), N2–P1–C13 107.49(16), C19–P1–C13 98.97(17), N4–P2–C43 11.43(16), N4–P2–C37 106.53(15), C43–P2–C37 99.63(15).

As already mentioned, the lithium atoms show different coordination environments. One lithium atom (Li2) is located in the center of a distorted tetrahedron and coordinated by two amide moieties and two pyridyl units. The other lithium cation (Li1) is situated in a trigonal-planar environment and binds to two nitrogen atoms and one tetrahydrofuran molecule. Similar structures of *N*-trialkylsilyl-substituted (2-pyridylmethyl)amides were observed earlier,[5] whereas lithium (diphenylphosphanyl)(2-pyridylmethyl)amide adopts a different structure.[28] The bridging fashion of the amide functionality and the higher coordination number of the nitrogen atoms lead to significant changes of the structural parameters. Nevertheless, rather short P–N bonds [165.7(3) and 165.9(3) pm] are observed in compound **3**, but in comparison to the free amine **2** they are only slightly shorter (Table 2). The reason for this shortening is the higher electrostatic attraction between the deprotonated amide function and the phosphanyl group.

Table 2. Selected average bond lengths [pm] and angles [°] of **2** and its lithium (**3**) and zinc derivative (**4**).

	2	**3**	**4**
N–H/Li/Zn	83	201.8	201.8
N–P	168.3	165.8	162.7
N–C	146.0	147.5	145.8
P–C^{I}	182.7	–	–
P–C^{II}	184.4	–	–
P–Zn	–	–	245.9
P–N–C	124.6	120.6	122.2
P–N–H/Zn	114	–	125.2
C–N–H/Zn	115	–	112.4
N–P–C^{I}	103.1	110.8	109.3
N–P–C^{II}	103.3	107.0	110.4
C^{I}–P–C^{II}	100.6	99.3	102.1
N–P–Zn	–	–	107.2
C^{I}–P–Zn	–	–	110.5
C^{II}–P–Zn	–	–	117.1

The molecular structure and numbering scheme of dimeric **4** is displayed in Figure 3. The zinc atoms are located in distorted tetrahedrons, and each binds to a methyl group, an amide moiety, a pyridyl unit, and a phosphorus atom. This fact leads to a large number of possible isomers, based on the chirality of the zinc atoms and of the tertiary carbon atoms C6A and C6B. However, the dimeric dinuclear complex exhibits nearly C_2 symmetry with a C_2 axis perpendicular to the six-membered $(ZnNP)_2$ ring. Due to this fact, both carbon atoms and both zinc atoms show the same configuration. Crystallization in a centrosymmetric space group leads to a racemate in the crystalline state.

Steric crowding hinders the formation of a four-membered Zn_2N_2 ring, and a six-membered $(ZnNP)_2$ cycle with a boat conformation is formed. This molecular structure is unique and stands in contrast to earlier reported structures of zincated (2-pyridylmethyl)amines in which the dimer is formed by means of a planar four-membered Zn_2N_2 ring.[1,2] The additional phenyl group puts a larger steric pressure on the molecule and forces dimerization through the phosphorus atoms. Despite the larger coordination number of the phosphorus

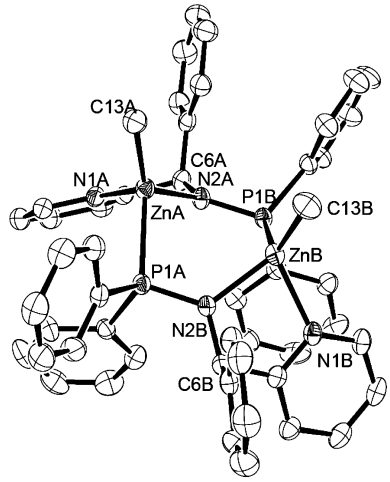
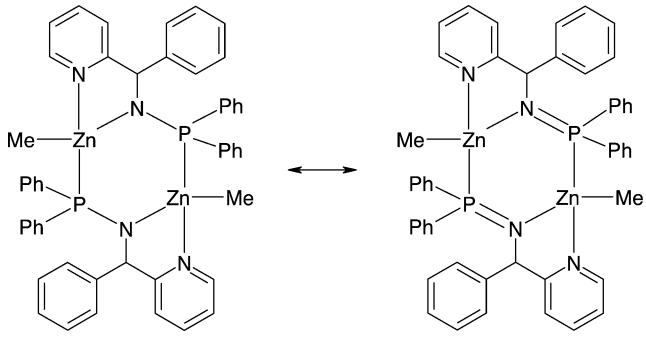


Figure 3. Molecular structure of dimeric **4**. The ellipsoids represent a probability of 40%. Aryl hydrogen atoms are omitted for reasons of clarity. The asymmetric unit contains one additional toluene molecule, which is not shown in this representation. Selected bond lengths [pm] and angles [°]: ZnA–C13A 198.3(3), ZnB–C13B 198.4(3), ZnA–N1A 213.8(2), ZnB–N1B 213.6(2), ZnA–N2A 201.4(2), ZnB–N2B 202.2(2), ZnA–P1A 246.21(8), ZnB–P1B 245.52(7) P1A–N2B 163.2(2) P1B–N2A 162.2(2) N2A–C6A 146.0(3) N2B–C6B 145.6(3); C13A–ZnA–N2A 126.87(11), C13–ZnA–N1A 119.00(12), N2A–ZnA–N1A 79.51(9), C13A–ZnA–P1A 119.33(9), N2A–ZnA–P1A 101.35(7), N1A–ZnA–P1A 102.37(7), C13B–ZnB–N2B 125.76(12), C13B–ZnB–N1B 119.49(13), N2B–ZnB–N1B 79.77(9), C13B–ZnB–P1B 121.02(11), N2B–ZnB–P1B 101.02(7), N1B–ZnB–P1B 100.62(6), C6A–N2A–P1B 121.52(18), C6A–N2A–ZnA 112.21(17), P1B–N2A–ZnA 125.96(13), C6B–N2B–P1A 122.79(18), C6B–N2B–ZnB 112.62(17), P1A–N2B–ZnB 124.37(13), N2B–P1A–C14A 109.36(13), N2B–P1A–C20A 111.00(12), C14A–P1A–C20A 102.25(13), N2B–P1A–Zn1A 107.56(8), C14A–P1A–Zn1A 110.16(9), C20A–P1A–Zn1A 116.33(10), N2A–P1B–C14B 109.31(13), N2A–P1B–C20B 109.78(13), C14B–P1B–C20B 102.00(13), N2A–P1B–Zn1B 106.74(8), C14B–P1B–Zn1B 110.92(9) C20B–P1B–Zn1B 117.89(9).

atoms, rather short P–N distances of 163.2(2) pm are observed. This finding can easily be explained by the mesomeric valence bond structures as shown in Scheme 3.



Scheme 3. Mesomeric valence bond presentations of dimeric **4**.

Conclusion

Ligand synthesis by means of metathesis reactions of lithiated (2-pyridylmethyl)amides with chlorophosphanes was improved by involving a very mild deprotonation protocol with triethylamine as a base. Subsequent reaction with chlorodiphenylphosphane allowed the synthesis of the desired *N*-substituted product **2** in very good yields and with high purity. According to crystal-structure analysis of the phosphanyl-substituted [α-(2-pyridyl)benzyl]amine, the planar amine functionality allows hyperconjugation and back-donation of electron density into antibonding P–C bonds.

Deprotonation of **2** with *n*-butyllithium in tetrahydrofuran yields a dinuclear lithium(I) complex, which is structurally related to the *N*-trialkylsilyl-substituted (2-pyridylmethyl)amides that crystallized from tetrahydrofuran. The zinc derivative **4** obtained from the zincation of **2** with $ZnMe_2$ forms a stable six-membered $(ZnNP)_2$ ring in a boat conformation, which is stabilized by a delocalization of the anionic charge within the P–N moieties.

Experimental Section

General Procedure: All manipulations were carried out under argon, and the solvents were thoroughly dried. IR spectra were recorded with Nujol solutions between KBr windows if not stated otherwise. The found N and C values of the elemental analyses deviate from calculated values because weighing of these moisture-sensitive compounds was challenging and also because of nitride and carbonate formation during combustion, even though V_2O_5 was added.

Synthesis of *N*-Hydroxy-1-phenyl-1-(2-pyridyl)methanimine: Phenyl (2-pyridyl) ketone (10.0 g, 54.6 mmol) and hydroxylamine hydrochloride (6.0 g, 86.0 mmol) were dissolved in a mixture of ethanol (40 mL) and water (4 mL). While the colorless suspension was stirred, solid sodium hydroxide (11.0 g, 275.0 mmol) was added stepwise. This suspension was stirred at room temp. for an additional 4 h, during which time the color of the solution turned yellowish. After addition of water (50 mL), the solution became clear. Dry ice was added until the oxime precipitated. All solids were collected and dried in vacuo. Yield: 9.91 g (50.0 mmol, 91%). M.p. 151 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.61 (s, 1 H, OH), 8.61 [d, ^3J(H,H) = 4.4 Hz, 1 H, H^1], 7.66 [dd, ^3J(H,H) = 7.6 Hz, 1 H, H^3], 7.55 [d, ^3J(H,H) = 8.0 Hz, 1 H, H^4], 7.44 (m, 5 H, PhH), 7.25 [dd, ^3J(H,H) = 4.4 Hz, 1 H, H^2] ppm. ^{13}C{^{1}H} NMR (50 MHz, $CDCl_3$): δ = 156.5 (C^6), 154.6 (C^5), 149.5 (C^1), 136.5 (C^3), 131.7 (C^7), 129.4 (C^8, C^{12}), 129.1 (C^{10}), 128.1 (C^9, C^{11}), 123.6 (C^2), 122.9 (C^4) ppm. MS (EI): *m*/*z* (%) = 198 (75) $[M]^+$, 181 (12) $[M - OH]^+$, 167 (100) $[M - NOH]^+$. IR (KBr pellet): $\tilde{\nu}$ = 3189 (vs), 3084 (s), 3060 (s), 3011 (m), 2926 (m), 1960 (vw), 1891 (vw), 1584 (s), 1566 (m), 1497 (w), 1469 (vs), 1442 (s), 1428 (s), 1328 (m), 1284 (w), 1246 (vw), 1178 (vw), 1152 (vw), 1095 (w), 1072 (vw), 1051 (w), 1034 (w), 1006 (vs), 993 (s), 946 (vs), 912 (m), 886 (vw), 791 (s), 771 (s), 744 (s), 702 (vs), 685 (m), 654 (w), 623 (w), 570 (vw), 490 (w), 469 (w) cm^{-1}. $C_{12}H_{10}N_2O$ (198.22): calcd. C 72.71, H 5.01, N 14.07; found C 72.24, H 5.08, N 14.13.

Synthesis of 1: *N*-Hydroxy-1-phenyl-1-(2-pyridyl)methanimine (9.9 g, 50 mmol) and ammonium acetate (2 g, 26 mmol) were dissolved in a mixture of a concentrated aqueous NH_3 solution (250 mL) and ethanol (50 mL). Then zinc dust (13 g, 200 mmol) was added. The resulting suspension was stirred at reflux for 2 h. After cooling to room temp., the excess amount of zinc was filtered off and washed with toluene. The filtrate was extracted with diethyl ether (3 × 50 mL). Then a 50% NaOH solution (10 mL) was added. This solution again was extracted with diethyl ether (2 × 50 mL). The ethereal fractions were combined, dried with Na_2SO_4, and the

solvents were removed in vacuo. The remaining oil was distilled in vacuo to yield a light yellow oily liquid. Yield: 6.0 g (32.7 mmol, 65%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.49 [d, ^3J(H,H) = 4.8 Hz, 1 H, H^1], 7.47 [dd, ^3J(H,H) = 7.6 Hz, 1 H, H^3], 7.36 [d, ^3J(H,H) = 8.4 Hz, 2 H, *o*-Ph], 7.24 [dd, ^3J(H,H) = 8.0 Hz, 2 H, *m*-Ph], 7.18 [d, ^3J(H,H) = 7.6 Hz, 1 H, H^4], 7.15 [dd, ^3J(H,H) = 4.0 Hz, 1 H, *p*-Ph], 7.02 [dd, ^3J(H,H) = 4.8 Hz, 1 H, H^2], 5.17 (s, 1 H, H^6), 2.14 (s, 2 H, NH_2) ppm. ^{13}C{^{1}H} NMR (50 MHz, $CDCl_3$): δ = 163.1 (C^5), 148.7 (C^1), 144.5 (C^7), 136.1 (C^3), 128.1 (C^9, C^{11}), 126.8 (C^8, C^{10}, C^{12}), 121.5 (C^2), 121.2 (C^4), 60.7 (C^6) ppm. MS (EI): *m*/*z* (%) = 184 (70) [M]$^+$, 168 (100) [M – NH_2]$^+$, 107 (94) [M – Ph]$^+$. IR (Nujol): $\tilde{\nu}$ = 3370 (w), 3270 (w), 3060 (w), 2924 (vs), 2854 (vs), 1925 (vw), 1901 (vw), 1588 (s), 1569 (m), 1492 (m), 1467 (s), 1433 (s), 1377 (m), 1266 (w), 1147 (w), 1046 (m), 1027 (m), 994 (m), 907 (w), 811 (m), 747 (s), 699 (s), 653 (w), 617 (w), 598 (w), 556 (w) cm^{-1}. $C_{12}H_{12}N_2$ (184.23): calcd. C 78.22, H 6.57, N 15.21; found C 77.66, H 6.57, N 15.01.

Synthesis of 2: Compound **1** (1.2 g, 6.6 mmol) was dissolved in toluene (20 mL), and then triethylamine (0.80 g, 8.0 mmol) was added. A solution of chlorodiphenylphosphane (1.46 g, 6.6 mmol) in toluene (10 mL) was added to this mixture, while stirring was continued at room temp. During the addition of the chlorodiphenylphosphane solution, colorless triethylamine hydrochloride precipitated. The reaction solution was stirred at room temperature overnight. The precipitate was removed, washed with toluene, and all volatiles were removed in vacuo, thus yielding a clear, almost colorless oily liquid. Yield: 2.3 g (6.3 mmol, 93%). ^{1}H NMR (400 MHz, C_6D_6): δ = 8.32 [d, ^3J(H,H) = 5.2 Hz, 1 H, H^1], 7.52 [dd, ^3J = 6.0 Hz, 4 H, *o*-CH^1(PPh_2)], 7.45 [dd, ^3J = 6.0 Hz, 4 H, *o*-CH^2(PPh_2)], 7.35 [d, ^3J(H,H) = 7.6 Hz, 2 H, *o*-Ph], 7.12–6.95 (m, 9 H, *m*,*p*-Ph, *m*,*p*-PPh_2), 6.86 [dd, ^3J(H,H) = 7.6 Hz, 1 H, H^3], 6.71 [d, ^3J(H,H) = 7.6 Hz, 1 H, H^4], 6.48 [dd, ^3J(H,H) = 4.8 Hz, 1 H, H^2], 5.48 [dd, ^3J(P,H) = 8.4 Hz, 1 H, CH], 4.36 [dd, ^2J(P,H) = 9.0, ^3J(H,H) = 5.0 Hz, 1 H, NH] ppm. ^{13}C{^{1}H} NMR (50 MHz, C_6D_6): δ = 162.7 [d, ^3J(C,P) = 6.3 Hz, C^5], 149.0 (C^1), 145.2 [d, ^3J(C,P) = 4.0 Hz, *i*-C(Ph)], 142.8 [d, ^1J(C,P) = 14.7 Hz, *i*-C(PPh_2)], 135.9 (C^3), 131.9 [d, ^1J(C,P) = 9.8 Hz, *o*-C^2(PPh_2)], 131.5 [d, ^1J(C,P) = 9.9 Hz, *o*-C^1(PPh_2)], 128.5–127.1 [*m*-C(PPh_2), *p*-C(PPh_2), *m*-C(Ph), *p*-C(Ph)], 122.1 (C^4), 121.6 (C^2), 65.8 [d, ^2J(C,P) = 22.4 Hz, C^6] ppm. ^{31}P{^{1}H} NMR (162 MHz, C_6D_6): δ = 42.2 ppm. MS (EI): *m*/*z* (%) = 368 (76) [M]$^+$, 200 (100) [M – HC(Py)(Ph)]$^+$, 183 (77) [M – PPh_2]$^+$, 168 (45) [M – HNPPh_2]$^+$. IR (neat): $\tilde{\nu}$ = 3348 (w), 3053 (s), 3025 (m), 2919 (w), 2849 (w), 1951 (vw), 1888 (vw), 1811 (vw), 1752 (vw), 1588 (s), 1569 (m), 1494 (m), 1476 (s), 1452 (m), 1433 (vs), 1392 (m), 1305 (w), 1282 (w), 1242 (w), 1184 (m), 1148 (m), 1089 (m), 1068 (m), 1047 (w), 1027 (m), 997 (m), 970 (w), 917 (w), 841 (w), 743 (vs), 696 (s), 636 (vw), 613 (w), 550 (w), 516 (m), 465 (m) cm^{-1}.

Synthesis of 3: A 1.6 M solution of *n*-butyllithium (0.46 mL) in hexane was added dropwise to a cooled (–78 °C) and stirred solution of **2** (0.27 g, 0.74 mmol) in thf (5 mL). After complete addition, the solution was slowly warmed to room temp. and stirred overnight. The solution color changed to deep brown. After removal of all volatiles, thf (2 mL) was added, and the desired compound crystallized at –78 °C within 2 d. Yield: 246 mg (0.30 mmol, 80%). M.p. 103 °C (dec.). ^{1}H NMR (200 MHz, C_6D_6): δ = 7.92 [d, ^3J(H,H) = 7.9 Hz, 1 H, H^1], 7.72 [d, ^3J(H,H) = 9.4 Hz, 2 H, *o*-Ph], 7.63 (m, 4 H, *o*-PPh_2), 7.16 [dd, ^3J(H,H) = 7.6 Hz, 2 H, *m*-Ph], 7.28 (m, 9 H, *m*-PPh_2), 6.98 (m, 1 H, *p*-PPh_2), 6.84 [dd, ^3J(H,H) = 7.4 Hz, 1 H, *p*-Ph], 6.68 [dd, ^3J(H,H) = 7.4 Hz, 1 H, H^3], 6.52 [d, ^3J(H,H) = 8.0 Hz, 1 H, H^4], 6.33 [dd, ^3J(H,H) = 5.8 Hz, 1 H, H^2], 5.76 [d, ^3J(H,P) = 21.4 Hz, 1 H, CH], 3.27 (m, 2 H, OCH_2), 1.24 (m, 2 H, CH_2) ppm. ^{13}C{^{1}H} NMR (50 MHz, C_6D_6): δ = 171.5 (br., C^5), 150.5 [*i*-C(Ph)], 148.3 [d, ^1J(C,P) = 30.0 Hz, *i*-C(PPh_2)], 147.5 (C^1), 136.2 (C^3), 133.1 [d, ^2J(C,P) = 20.3 Hz, *o*-C(PPh_2)], 129.1 [*o*-C(Ph)], 126.9 [*m*-C(PPh_2)], 126.7 [*p*-C(PPh_2)], 128.3 [*m*-C(Ph)], 125.8 [*p*-C(Ph)], 123.7 (C^4), 120.6 (C^2), 71.6 [d, ^2J(C,P) = 13.7 Hz, CH], 67.9 (OCH_2) 25.5 (CH_2) ppm. ^{31}P{^{1}H} NMR (81 MHz, C_6D_6): δ = 52.4 ppm. ^{7}Li NMR (149 MHz, [D_6]benzene): δ = 3.1 (LiN_4), 1.6 (LiN_2O) ppm. IR (Nujol): $\tilde{\nu}$ = 3165 (vw), 3136 (vw), 3053 (m), 2924 (vs), 2854 (vs), 2722 (vw), 2669 (vw), 2607 (vw), 2048 (vw), 1957 (w), 1884 (w), 1809 (vw), 1766 (vw), 1722 (vw), 1660 (vw),

Table 3. Crystal data and refinement details for the X-ray structure determinations of **2**, **3**, and **4**.

	2	**3**	**4**
Empirical formula	$C_{24}H_{21}N_2P$	$C_{52}H_{48}Li_2N_4OP_2{\cdot}C_4H_8O$	$C_{50}H_{46}N_4P_2Zn_2{\cdot}C_7H_8$
M_r [g mol^{-1}]	368.39	892.87	987.72
T [K]	183(2)	183(2)	183(2)
Crystal system	triclinic	monoclinic	triclinic
Space group	$P\bar{1}$ (no. 2)	$P2_1/n$ (no. 14)	$P\bar{1}$ (no. 2)
a [Å]	9.393(1)	10.2964(2)	12.9680(4)
b [Å]	9.846(1)	27.6523(8)	13.9220(5)
c [Å]	12.248(1)	18.7652(5)	16.0896(7)
α [°]	85.009(5)	90	86.320(2)
β [°]	71.571(5)	92.916(2)	74.334(2)
γ [°]	65.452(6)	90	63.121(2)
V [Å^3]	976.14(18)	5335.9(2)	2489.21(16)
Z	2	4	2
ρ [g cm^{-3}]	1.250	1.103	1.318
μ [cm^{-1}]	1.5	1.23	10.69
Measurement range [°]	$4.56 < 2\theta < 54.88$	$4.22 < 2\theta < 54.96$	$4.34 < 2\theta < 55.00$
Measured data	6457	33780	17823
Unique data (R_{int})	4685	12173	11310
Data with $I > 2\sigma(I)$	2826	6855	8575
wR_2 (all data, on F^2)[a]	0.1683	0.2897	0.1185
R_1 [$I > 2\sigma(I)$][a]	0.0632	0.0876	0.0707
s[b]	1.020	1.020	1.008
Residual density [e Å^{-3}]	0.533/–0.629	0.996/–0.391	1.182/–0.413

[a] Definition of the R indices: $R1 = (\Sigma||F_o| - |F_c||)/\Sigma|F_o|$; $wR^2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$ with $w^{-1} = \sigma^2(F_o^2) + (aP)^2 + bP$; $P = [2F_c^2 + \max(F_o^2)]/^3$. [b] $S = \{\Sigma[w(F_o^2 - F_c^2)^2]/(N_o - N_p)\}^{1/2}$.

1592 (m), 1569 (m), 1454 (vs), 1377 (vs), 1341 (w), 1306 (w), 1279 (w), 1248 (w), 1195 (w), 1152 (w), 1124 (w), 1110 (w), 1070 (w), 1046 (w), 1027 (w), 998 (w), 974 (w), 942 (w), 917 (w), 884 (w), 860 (w), 843 (w), 737 (m), 722 (m), 697 (m), 666, (vw), 647 (vw), 614 (vw), 543 (w), 515 (w) cm^{-1}. $C_{52}H_{48}Li_2N_4OP_2$ (820.75): calcd. C 76.10, H 5.90, N 6.83; found C 72.42, H 5.18, N 6.63.

Synthesis of 4: Compound **2** (0.40 g, 1.1 mmol) was dissolved in toluene (3 mL) and cooled to 0 °C. A 1.5 M solution of dimethylzinc (0.75 g) in toluene was added dropwise to this stirred solution. After addition, the color of the solution changed to deep violet. This clear solution was stirred at room temp. for an additional 2 h. After removal of the solvent (2 mL) in vacuo, the remaining solution was stored at –20 °C. The crystalline, colorless product was obtained from this solution after storage at –20 °C for several days. Yield: 0.33 g (0.75 mmol, 68%). ^{1}H NMR (400 MHz, [D$_8$]thf): δ = 8.02 [d, ^3J(H,H) = 4.0 Hz, 1 H, H^1] 7.49 [dd, ^3J(H,H) = 8.0 Hz, 1 H, H^3], 7.32 (m, 2 H, *o*-Ph), 7.17 (m, 4 H, *o*-PPh$_2$), 7.02 (m, 6 H, *m*-PPh$_2$, *p*-PPh$_2$), 6.90 (m, 3 H, *m*-Ph, *p*-Ph), 7.05 (m, 1 H, H^4), 6.94 (m, 1 H, H^2), 5.46 [d, ^3J(H,P) = 17.2 Hz, 1 H, CH], –0.61 (s, 3 H, CH$_3$) ppm. ^{13}C{^{1}H} NMR (100 MHz, [D$_8$]thf): δ = 166.2 (br., C^5), 145.9 [*i*-C(Ph)], 147.3 (C^1), 147.8 [br., *i*-C(PPh$_2$)], 138.5 (C^3), 133.5 [d, ^2J(C,P) = 13.2 Hz, *o*-C(PPh$_2$)], 133.0 [d, ^2J(C,P) = 14.3 Hz, *o*-C(Ph)], 128.5 [*m*-C(PPh$_2$), *p*-C(PPh$_2$)], 127.9 [*m*-C(Ph), *p*-C(Ph)], 123.7 (C^4), 122.7 (C^2), 67.7 [d, ^2J(C,P) = 20.8 Hz, C^6], –11.8 (CH$_3$) ppm. ^{31}P{^{1}H} NMR (81 MHz, C$_6$D$_6$): δ = 46.8 ppm. IR (Nujol): $\tilde{\nu}$ = 2924 (vs), 2854 (vs), 1603 (w), 1450 (m), 1437 (m), 1377 (w), 1304 (vw), 1264 (vw), 1195 (w), 1152 (w), 1080 (w), 1042 (m), 1019 (w), 802 (vw), 759 (m), 703 (w), 687 (w), 665 (w), 619 (w), 572 (vw), 509 (vw) cm^{-1}. $C_{50}H_{46}N_4P_2Zn_2$ (895.60): calcd. C 67.05, H 5.18, N 6.26; found C 66.10, H 5.63, N 6.03.

Structure Determinations: The intensity data for the compounds were collected with a Nonius KappaCCD diffractometer by using graphite-monochromated Mo-K_α radiation.[29,30] The structures were solved by Direct Methods (SHELXS[31]) and refined by full-matrix least-squares techniques against F_o^2 (SHELXL-97[32]). All hydrogen atoms were included at calculated positions with fixed thermal parameters. All nondisordered non-hydrogen atoms were refined anisotropically.[32] Crystallographic data as well as structure solution and refinement details are summarized in Table 3. The XP program (Siemens Analytical X-ray Instruments, Inc.) was used for structure representations. CCDC-761465 (**2**), -761466 (**3**), and -761467 (**4**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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