Organometallics **2005,** *24,* 5287−5293

Zwitterionic and Bis-amido Zinc Complexes with Bulky Bis(phosphanylamino)benzene Ligands: Synthesis, Reactivity, and Molecular Structures of $[ZnCl_2(1,2\text{-}\{N(PHMes_2)\}_2C_6H_4\text{-}\kappa^2N,N')]$, $[ZnPr\{1\text{-}N(PMes_2)\text{-}2\text{-}N(PHMes_2)C_6H_4\text{-}\kappa^2N,N'\}]$, and $[Zn\{1\text{-}N(PMes_2)\text{-}2\text{-}N(\mu\text{-}PMes_2)C_6H_4\text{-}\kappa^3N,N',P\}]_2$

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Received May 19, 2005

The reaction of $[ZnCl_2(THF)_2]$ with $1,2\text{-}\{NH(PMes_2)\}_2C_6H_4$ (Mes = $2,4,6\text{-}Me_3C_6H_2$) yielded the unusual Zn^{II} complex $[ZnCl_2(1,2\text{-}\{N(PHMes_2)\}_2C_6H_4\text{-}\kappa^2N,N')]$ (**1**), in which a proton transfer from nitrogen to phosphorus had occurred. ZnR_2 reacted with $1,2\text{-}\{NH(PMes_2)\}_2C_6H_4$ to give the zwitterionic compounds $[ZnR\{1\text{-}N(PMes_2)\text{-}2\text{-}N(PHMes_2)C_6H_4\text{-}\kappa^2N,N'\}]$ (R = Pr (**2a**), Et (**2b**)). The bis-amido complex $[Zn\{1\text{-}N(PMes_2)\text{-}2\text{-}N(\mu\text{-}PMes_2)C_6H_4\text{-}\kappa^3N,N',P\}]_2$ (**3**) was obtained from $ZnCl_2$ and $1,2\text{-}\{LiN(PMes_2)\}_2C_6H_4$. The Zn^{II} alkoxide complex $[Zn\{1\text{-}N\{PMes_2\text{-}CH_2CH(Me)O\}\text{-}2\text{-}N(PMes_2)C_6H_4\text{-}\kappa^3N,N',O\}]_2$ (**4**) was obtained from the reaction of **2a** with propylene oxide. Complexes **1**−**4** were characterized spectroscopically (^1H, ^{13}C, ^{31}P NMR; MS; IR) and by X-ray structure determination.

Introduction

Tertiary phosphines have long been the most commonly employed ligands in the synthesis of transition metal complexes in low oxidation states with catalytic properties, for example, group 10 metals and rhodium.[1] There is increasing interest in the use of bis(aminophosphine) ligands to generate new organometallic compounds or catalytically active complexes.[2−4] The presence of two different donor atoms, phosphorus and nitrogen, in the organic molecule is responsible for very different chemical and physical properties, both of the bis(aminophosphine) itself and of the complexes that result from its coordination to a metal. Lately, a new field based on the utilization of secondary aminophosphine ligands in catalysis has been opened up,[5] and some secondary bis(aminophosphines) derived from *o*-phenylenediamine and their use as ligands in complexes of Pd, Pt, Mo, and Au,[6,7,8] as well as the Ni^0 complex $[Ni(PPh_2NHPh)_4]$[9] and the Mo^0 complex *cis*-$[Mo(CO)_4(PPh_2NHR)_2]$[10] (R = Ph, ^tBu), have been reported. Moreover, nickel 1,2-diiminophosphorane complexes with nitrogen as donor atoms also exhibit catalytic activity in ethylene oligomerization.[11]

However, the coordination chemistry of bis(aminophosphine) ligands with main group metals and nitrogen as donor atom has hardly been explored, and zinc complexes of bis(aminophosphines) have also received only limited attention. Amido zinc complexes generally adopt polymeric structures in the solid state,[12] but with a bulky substituent on nitrogen, monomeric[13] and low-coordinate[14] zinc complexes with catalytic properties[15] were obtained. By tailoring the coordination environment of the zinc center, some zinc(II) complexes were

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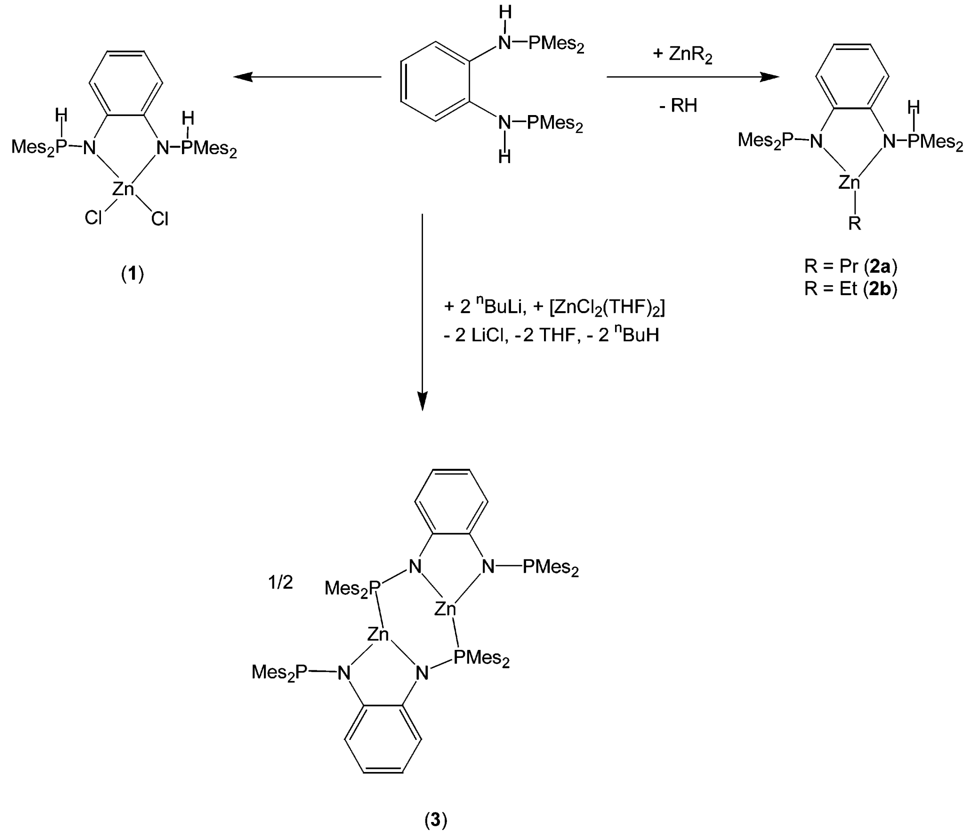
Scheme 1



found to be single-site catalysts that can control the molecular weight of the polycarbonate formed from the alternating copolymerization of CO_2 and epoxides.[16]

In our search for potential bi- and oligodentate ligands based on phosphanylamines and -amides for use in transition and main group metal complexes, we reported the bulky 1,3-$\{N(PPh_2)_2\}_2C_6H_4$[17] and 1,2-$\{NH(PMes_2)\}_2C_6H_4$[18,19] and their Mo and Ni complexes. We now report on the synthesis and characterization of a series of Zn^{II} complexes $[ZnCl_2(1,2\text{-}\{N(PHMes_2)\}_2C_6H_4\text{-}\kappa^2N,N')]$ (**1**), $[ZnR\{1\text{-}N(PMes_2)\text{-}2\text{-}N(PHMes_2)C_6H_4\text{-}\kappa^2N,N'\}]$ (R = Pr (**2a**), Et (**2b**)), and $[Zn\{1\text{-}N(PMes_2)\text{-}2\text{-}N(\mu\text{-}PMes_2)C_6H_4\text{-}\kappa^3N,N',P\}]_2$ (**3**) based on the secondary bulky bis(phosphanylamine) 1,2-$\{NH(PMes_2)\}_2C_6H_4$ ligand framework. The Zn^{II} alkoxide complex $[Zn\{1\text{-}N\{PMes_2CH_2CH(Me)O\}\text{-}2\text{-}N(PMes_2)C_6H_4\text{-}\kappa^3N,N',O\}]_2$ (**4**), obtained from the reaction of **2a** with propylene oxide, is also reported.

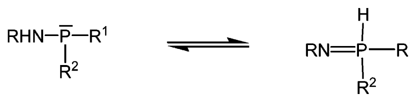
Results and Discussion

Synthesis and Spectroscopic Properties of $[ZnCl_2(1,2\text{-}\{N(PHMes_2)\}_2C_6H_4\text{-}\kappa^2N,N')]$ (1), $[ZnR\{1\text{-}N(PMes_2)\text{-}2\text{-}N(PHMes_2)C_6H_4\text{-}\kappa^2N,N'\}]$ (R = Pr (2a), Et (2b)), and $[Zn\{1\text{-}N(PMes_2)\text{-}2\text{-}N(\mu\text{-}PMes_2)C_6H_4\text{-}\kappa^3N,N',P\}]_2$ (3). 1,2-$\{NH(PMes_2)\}_2C_6H_4$[18] reacts with 1 equiv of $[ZnCl_2(THF)_2]$ in CH_2Cl_2 to give the mononuclear compound $[ZnCl_2(1,2\text{-}\{N(PHMes_2)\}_2C_6H_4\text{-}\kappa^2N,N')]$ (**1**) (Scheme 1).

Alkane elimination with formation of the bis-amido complex $[Zn(1,2\text{-}\{N(PMes_2)\}_2C_6H_4\text{-}\kappa^2N,N')]$ was expected in the reaction of 1,2-$\{NH(PMes_2)\}_2C_6H_4$ with ZnR_2 in toluene or THF. However, only 1 equiv of propane (or ethane) was eliminated and the unusual tricoordinate mononuclear compounds $[ZnR\{1\text{-}N(PMes_2)\text{-}2\text{-}N(PHMes_2)C_6H_4\text{-}\kappa^2N,N'\}]$ (R = Pr (**2a**), Et (**2b**)) (Scheme 1) were obtained in good yield.

The bis-amido complex $[Zn(1,2\text{-}\{N(PMes_2)\}_2C_6H_4\text{-}\kappa^2N,N')]$ was obtained from the reaction of the anionic ligand $[1,2\text{-}\{N(PMes_2)\}_2C_6H_4]^{2-}$, prepared in situ from 1,2-$\{NH(PMes_2)\}_2C_6H_4$ and 2 equiv of ^nBuLi in THF at −78 °C, with $[ZnCl_2(THF)_2]$ at room temperature. The bis-amido complex $[Zn\{1\text{-}N(PMes_2)\text{-}2\text{-}N(\mu\text{-}PMes_2)C_6H_4\text{-}\kappa^3N,N',P\}]_2$ (**3**) shows an unusual association via phosphine bridges to give a dinuclear structure (Scheme 1).

In the ^{31}P NMR spectrum of **1**, the single doublet observed at −4.5 ppm with $^1J_{PH} = 461$ Hz indicates a proton transfer from nitrogen to phosphorus. This tautomerism is well known in aminophosphines and can lead to imidophosphoranes:[20]



$$RHN\text{-}\overline{P}(R^2)\text{-}R^1 \rightleftharpoons RN{=}P(H)(R^2)\text{-}R^1$$

The presence of electron-donating groups on phosphorus and electron-withdrawing groups on nitrogen can tilt the balance in favor of P being more basic than N, as was observed in **I**, in which the proton migrated from nitrogen to phosphorus, and the $\nu(P{=}N)$ vibration was assigned to a band at 1140 cm^{-1}.[21] Apparently,

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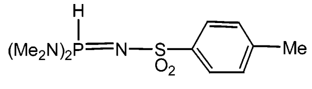
upon coordination to the Lewis acidic zinc, the phosphorus atoms in **1** become more basic than nitrogen.



(I)

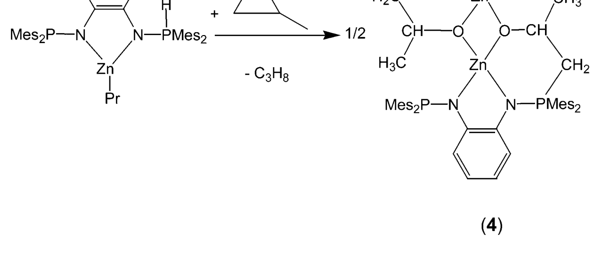
In the ^{31}P NMR spectra, compounds **2a** and **2b** show two different phosphorus chemical shifts at 43.0 ppm (s) and −5.2 ppm (d, $^1J_{PH}$ = 459 Hz) and 43.1 ppm (s) and −5.2 ppm (d, $^1J_{PH}$ = 458.5 Hz) due to a proton transfer from N to P similar to that in the case of compound **1**. The steric effect of the ligand was confirmed by performing the reaction of $ZnPr_2$ with 1,2-$\{NH(PPh_2)\}_2C_6H_4$, which has phenyl substituents on the phosphorus atoms. In this reaction, both alkyl groups were eliminated as propane, and the dimeric complex $[Zn\{1\text{-}N(PPh_2)\text{-}2\text{-}N(\mu\text{-}PPh_2)C_6H_4\text{-}\kappa^3 N,N',P\}(THF)]_2$ was obtained in which zinc is in a tetrahedral environment with coordination of two additional THF solvent molecules.[19]

In the ^{31}P NMR spectrum of **3** in THF/C_6D_6 at room temperature, two different phosphorus chemical shifts are observed, as expected; however, their ratio is ca. 1:3. The singlet at 23.2 ppm is assigned to the coordinated P atom, and the broad singlet at 37.9 ppm, indicative of an exchange process in solution, is assigned to the free P atom. At room temperature, this exchange between the coordinated phosphorus atom and THF is rapid on the NMR time scale. When the ^{31}P NMR spectrum in C_4D_8O is measured at 255 K, the dynamic process is frozen and two sharp singlets of equal intensity are obtained at 36 ppm (for P-Mes) and 21.2 ppm (for P-Zn).

In the ^{1}H NMR spectrum, a doublet is observed for the PH protons at 8.43 ppm (for **1**, $^1J_{PH}$ = 461 Hz) or 8.33 ppm (for **2a** and **2b**, $^1J_{PH}$ = 459 and 458.5 Hz). In the ^{1}H NMR spectrum, the CH_2-Zn protons are observed at −0.53 ppm (for **2a**) and −0.51 ppm (for **2b**).

In the IR spectra of **1**, **2a**, and **2b**, the ν(PH) vibration is observed at ca. 2350 cm^{-1}, respectively. The ν(P=N) vibration in **1**, **2a**, and **2b** is assigned to a strong band at ca. 1125 cm^{-1}; ν(PN) in **2a**, **2b**, and **3** is observed at ca. 910 cm^{-1}, respectively. Monophosphazenes exhibit ν(P=N) vibrations in the range 1147−1500 cm^{-1}.[22]

Reaction of 2a with Propylene Oxide and Characterization of $[Zn\{1\text{-}N\{PMes_2CH_2CH(Me)O\}\text{-}2\text{-}N(PMes_2)C_6H_4\text{-}\kappa^3 N,N',O\}]_2$ (4). The ring-opening reaction of propylene oxide with the Zn complex **2a** in toluene gives the dinuclear compound **4** (eq 1).



(**4**) (1)

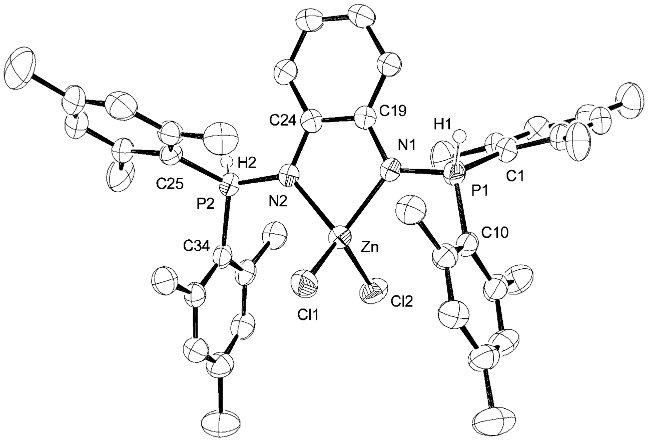
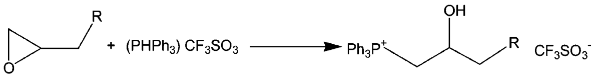


Figure 1. Molecular structure of **1** (ORTEP plot, H atoms other than P-H omitted for clarity; thermal ellipsoids set at 50% probability).

We assume that the reaction is initiated by the PH group, based on a report by Mironov et al.[23] that triphenylphosphonium triflate opens epoxides (eq 2):



(2)

In the ^{31}P NMR spectrum, compound **4** shows only two signals at 16.3 and 10.8 ppm, indicating that only one diastereomer is present. The signal at 16.3 ppm is attributed to the pendant N-$PMes_2$ group and the signal at 10.8 ppm to the phosphorus atom in the six-membered ring. In the IR spectrum, the ν(PN) vibrations are observed at 1119 and 932 cm^{-1}, i.e., shifted to higher wavenumber in comparison with that of **2a** (909 cm^{-1}).

Molecular Structures of 1, 2a, 3, and 4. Compound **1** (Figure 1) crystallizes in the monoclinic system, space group *C*2/*c* with eight molecules and four noncoordinating THF molecules in the unit cell; compound **2a** (Figure 2) crystallizes orthorhombic in the noncentrosymmetric space group *Pca*2$_1$ with four molecules in the unit cell. Selected bond lengths and angles are listed in Tables 1 and 2.

Compounds **1** and **2a** are mononuclear complexes with five-membered chelate rings formed by coordination of both nitrogen atoms. The zinc atom in **1** is coordinated in a distorted tetrahedral fashion by two nitrogen atoms and two chloride ligands, while in **2a**, the zinc atom is in a trigonal-planar environment (sum of the bond angles is 360.1°), coordinated by two nitrogen atoms and one propyl group. In accordance with the NMR spectroscopic data, the crystal structures of **1** and **2a** confirm the proton transfer from nitrogen to phosphorus. The P−N bond lengths of 1.603(3) and 1.601(3) Å in **1** are in the range found for imidophosphorane complexes of Zn and Co where N is the donor

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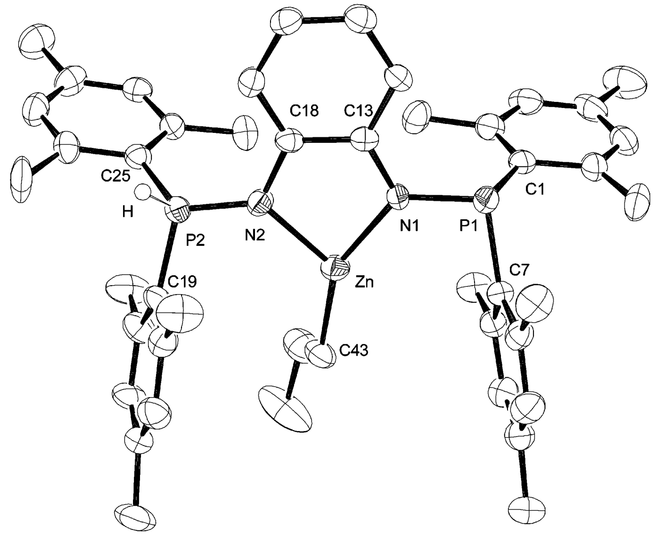

Figure 2. Molecular structure of **2a** (ORTEP plot, H atoms other than P-H omitted for clarity; thermal ellipsoids set at 50% probability).

Table 1. Selected Bond Lengths (Å) and Angles (deg) for 1

P(1)−N(1)	1.603(3)	C(24)−N(2)−Zn	112.1(2)
P(2)−N(2)	1.601(3)	P(2)−N(2)−Zn	125.7(2)
Zn−N(1)	2.037(3)	C(10)−P(1)−C(1)	113.9(2)
Zn−N(2)	2.044(3)	N(1)−P(1)−C(10)	108.1(2)
Zn−Cl(1)	2.246(1)	N(1)−P(1)−C(1)	117.5(2)
Zn−Cl(2)	2.241(1)	N(2)−P(2)−C(34)	108.02(1)
N(1)−Zn−N(2)	82.3(1)	N(2)−P(2)−C(25)	118.6(2)
N(1)−Zn−Cl(1)	115.50(8)	C(34)−P(2)−C(25)	114.3(2)
N(2)−Zn−Cl(2)	115.44(8)	P(1)−N(1)−Zn	125.8(2)
C(19)−N(1)−P(1)	121.9(2)	C(24)−N(2)−P(2)	122.1(2)
C(19)−N(1)−Zn	112.3(2)		

Table 2. Selected Bond Lengths (Å) and Angles (deg) for 2a

P(1)−N(1)	1.706(4)	P(1)−N(1)−Zn	129.0(2)
P(2)−N(2)	1.611(4)	C(18)−N(2)−Zn	110.5(3)
Zn−N(1)	1.933(3)	C(18)−N(2)−P(2)	119.3(3)
Zn−N(2)	2.034(4)	P(2)−N(2)−Zn	130.1(2)
Zn−C(43)	1.966(5)	C(1)−P(1)−C(7)	103.1(2)
N(1)−Zn−N(2)	84.6(2)	N(1)−P(1)−C(7)	100.2(2)
N(1)−Zn−C(43)	149.7(2)	N(1)−P(1)−C(1)	110.2(2)
N(2)−Zn−C(43)	125.7(2)	N(2)−P(2)−C(25)	117.7(2)
C(13)−N(1)−P(1)	117.0(3)	N(2)−P(2)−C(19)	108.1(2)
C(13)−N(1)−Zn	112.9(3)	C(25)−P(2)−C(19)	114.4(2)

atom, e.g., [$ZnCl_2\{N(SiMe_3)PMe_3\}_2$] [1.606(3), 1.603(3) Å] and [$CoCl_2(NHPMe_3)_2$] [1.602(7), 1.597(9) Å],[24] and in iminophosphoranes [1.596−1.631 Å][25] in which double-bond character of the PN bond is assumed. Similarly, in **2a** the P(2)−N(2) distance of 1.611(4) Å indicates double-bond character and the presence of an iminophosphorane group ($Mes_2PH{=}NR$), while the P(1)−N(1) bond of the phosphanylamino group is longer [1.706(4) Å]. In **1**, the Zn−N and Zn−Cl bond lengths are in the same range as observed for the tetrahedral Zn amine complex [$ZnCl_2(NH_2CH_2CMe_2CH_2NH_2)$][26] [2.018(1) and 2.212(1) Å]. In **2a**, the Zn−N(1) bond length of 1.933(3) Å is smaller than the Zn−N(2) bond length of 2.034(4) Å, and this supports the assumption of an amido [Zn−N(1)] and an iminophosphorane [Zn−N(2)] group. The geometry around the coordinated nitrogen atoms in **1** and **2a** is essentially planar (sums of the bond angles at N(1) and N(2) 359.0−360.0°). The N(1)−Zn−N(2) bond angle of 84.6(2)° in **2a** is only slightly larger than in the tetrahedral Zn complex **1** [82.3(1)°] and is in the range observed for other zinc chelate complexes with a similar environment (80.7−84.4°).[27] In the tetranuclear zinc ethyl complex [$\{(\pm)$-*trans*-cyclo-$C_6H_{10}(NSiMe_3)_2\}_2$-Zn_4Et_4], which has three-coordinate zinc atoms, a larger N−Zn−N bond angle of 91.0(1)° was observed.[28] In **2a**, the C(13)−N(1)−Zn and C(13)−N(1)−P(1) bond angles of 112.9(3)° and 117.0(3)° are smaller than the P(1)−N(1)−Zn bond angle of 129.0(2)° due to the chelating bonding mode of the ligand. Similarly, at N(2), two bond angles are smaller than the third. The Zn−C(43) distance of 1.966(5) Å is in the same range as obtained for the three-coordinate β-diiminato Zn ethyl complex [1.963(5) Å][11] and related compounds.[29]

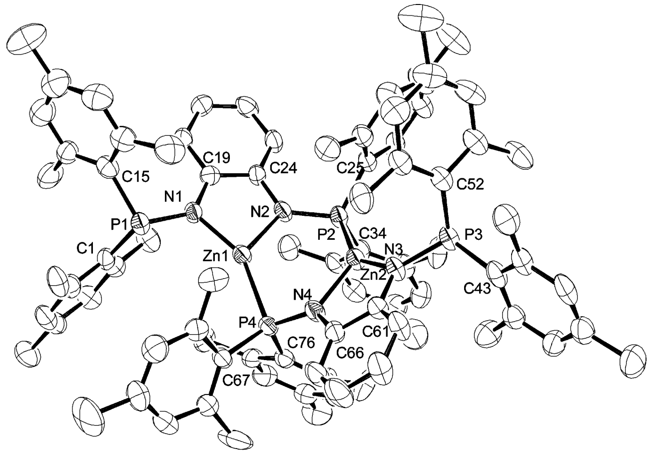

Figure 3. Molecular structure of **3** (H atoms omitted for clarity; thermal ellipsoids set at 50% probability).

Table 3. Selected Bond Lengths (Å) and Angles (deg) for 3

N(1)−P(1)	1.696(5)	P(2)−Zn(2)	2.329(2)
N(2)−P(2)	1.644(5)	P(4)−Zn(1)	2.311(2)
N(3)−P(3)	1.698(5)	N(3)−Zn(2)−N(4)	87.6(2)
N(4)−P(4)	1.643(5)	N(3)−Zn(2)−P(2)	148.9(2)
Zn(1)−N(1)	1.900(5)	N(4)−Zn(2)−P(2)	123.3(2)
Zn(1)−N(2)	1.953(5)	N(1)−Zn(1)−N(2)	87.9(2)
Zn(2)−N(3)	1.904(5)	N(1)−Zn(1)−P(4)	150.2(2)
Zn(2)−N(4)	1.956(5)	N(2)−Zn(1)−P(4)	121.9(2)

Compound **3** crystallizes in the triclinic space group $P\bar{1}$ with two molecules and four noncoordinating THF molecules in the unit cell. Selected bond lengths and angles are listed in Table 3. The molecular structure of **3** (Figure 3) shows a dimer in which each zinc atom is coordinated by two nitrogen atoms and one phosphorus atom. The N atoms bound to Zn form two five-membered chelate rings, and two of the four phosphorus atoms (P(2) and P(4)) bridge the two chelate rings. As in **2a**, for steric reasons, the coordination environment at the metal centers is distorted trigonal-planar (the sums of

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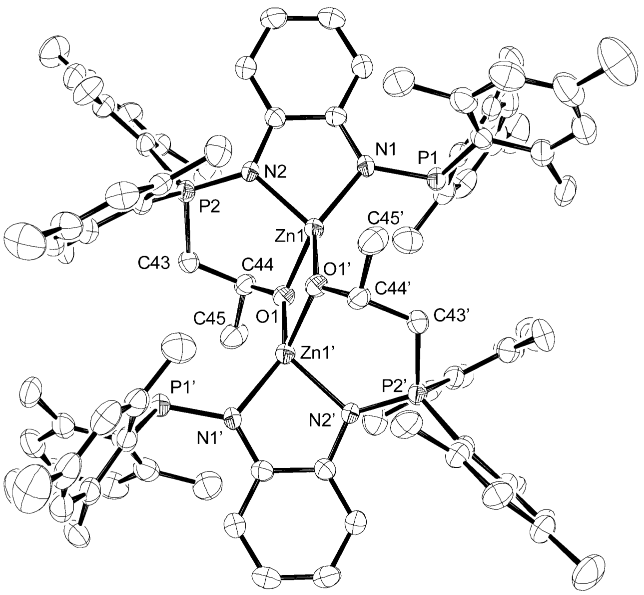

Figure 4. Molecular structure of **4** (H atoms omitted for clarity; thermal ellipsoids set at 50% probability).

Table 4. Selected Bond Lengths (Å) and Angles (deg) for 4

Zn(1)−N(1)	1.940(3)	Zn(1)−O(1′)	1.965(3)
Zn(1)−O(1)	1.984(3)	Zn(1)−N(2)	2.058(3)
P(1)−N(1)	1.681(3)	P(2)−N(2)	1.602(3)
P(2)−C(43)	1.838(4)	O(1)−C(44)	1.415(5)
		N(1)−Zn(1)−O(1′)	129.0(1)
O(1′)−Zn(1)−O(1)	80.9(1)	N(1)−Zn(1)−N(2)	85.0(1)
O(1)−Zn(1)−N(2)	98.8(1)	C(44)−O(1)−Zn(1′)	132.9(2)
C(44)−O(1)−Zn(1)	116.6(2)	Zn(1′)−O(1)−Zn(1)	99.1(1)

bond angles at Zn are 360.1° and 359.9°), and this is unusual, as zinc is often found to prefer a tetrahedral environment. The N(1)−Zn(1)−N(2) and N(3)−Zn(2)−N(4) bond angles of 87.9(2)° and 87.6(2)° are larger than in the monomeric Zn complex **2a** (84.6(2)°), probably due to the bridging phosphorus atoms. The atoms N(1), N(2), N(3), and N(4) have a trigonal-planar environment (sums of bond angles 359.4−360.0°). The Zn(1)−N(1) and Zn(2)−N(3) bond lengths of 1.900(5) and 1.904(5) Å of the five-membered rings are smaller than the Zn(1)−N(2) and Zn(2)−N(4) bond lengths of 1.953(5) and 1.956(5) Å, which are comparable to complex **2a**. They correspond to the smaller P(2)−N(2) and P(4)−N(4) bond lengths of 1.644(5) and 1.643(5) Å for the bridging phosphorus atoms and the larger P(1)−N(1) and P(3)−N(3) bond lengths of 1.696(5) and 1.698(5) Å for the free phosphines, respectively. The P(2)−Zn(2) and P(4)−Zn(1) bond lengths of 2.329(2) and 2.311(2) Å are smaller than the bond lengths of 2.369(1) and 2.384(1) Å observed in the monomeric Zn complex $[ZnCl_2(PMe_3)_2]$.[30]

Compound **4** crystallizes in the triclinic space group $P\bar{1}$ with one centrosymmetric molecule in the unit cell and four toluene molecules in the unit cell. Selected bond lengths and angles are listed in Table 4. The crystal structure of **4** (Figure 4) shows a centrosymmetric dimeric dinuclear Zn complex with bridging alkoxide groups, in which one P atom has participated in the regioselective ring-opening reaction of the epoxide at the sterically less hindered carbon atom. Only the *R*,*S* diastereomer is present in the crystal structure due to the presence of an inversion center in the molecule. The molecule adopts a planar geometry for the Zn_2O_2 core, which is part of two six-membered rings formed by the propyloxide group and the P−N group of the ligand. The Zn(1)−O(1′) and Zn(1)−O(1) bond lengths of 1.965(3) and 1.984(3) Å are comparable to those observed in known zinc alkoxide complexes with β-diiminato ligands [1.983(3) to 1.931(2) Å].[15b,16] A distorted tetrahedral geometry with a N−Zn−N bite angle of 85.0(1)° is observed for the Zn center. The O(1)−Zn(1)−O(1′) bond angle of 80.9(1)° is comparable to those found in the dinuclear zinc complex $[ZnO^{i}Pr(\{N(2,6\text{-}^{i}Pr_2C_6H_3)CMe\}_2CH)]_2$ [78.5(1)° and 81.83(9)°].[15b] The P(2)−N(2) distance of 1.602(3) Å is smaller than the P(1)−N(1) distance of 1.681(3) Å, and this indicates double-bond character due to delocalization of the nitrogen lone pair, as observed in Zn complex **2a**.

Conclusions

In conclusion, we have presented a new family of Zn bisamido complexes, of which especially the three-coordinate zinc alkyl complexes **2a**,**b** are of interest. Here, a ring-opening reaction of propylene oxide with **2a** to give a Zn^{II} alkoxide complex was observed. In addition, complex **2a** can effectively be used for the rapid polymerization of lactones to polyesters.[31]

Experimental Section

General Details. All operations were carried out under a dry nitrogen atmosphere using standard Schlenk techniques. The reagents and solvents were purified by standard procedures. The ^{1}H, ^{13}C, and ^{31}P NMR spectra were recorded on an AVANCE DRX 400 spectrometer (Bruker). ^{1}H NMR (400.13 MHz): internal standard TMS; ^{13}C NMR (100.6 MHz): internal standard TMS; ^{31}P NMR (161.9 MHz): external standard 85% H_3PO_4. The IR spectra were recorded on a Perkin-Elmer System 2000 (KBr) FTIR spectrometer in the range 350−4000 cm^{-1}. The FAB mass spectra were recorded on a ZAB-HSQ-VG Analytical Manchester. Elemental analyses were performed on a VARIO EL (Heraeus) with handling of samples in air. The crystal data were measured on a Siemens SMART CCD diffractometer. $1,2\text{-}\{NH(PMes_2)\}_2C_6H_4$,[18] $[ZnCl_2(THF)_2]$,[32] and $ZnPr_2$[33] were prepared by literature procedures. Propylene oxide and $ZnEt_2$ are commercially available.

Preparation of $[ZnCl_2(1,2\text{-}\{N(PHMes_2)\}_2C_6H_4\text{-}\kappa^2N,N')]$ (1). $1,2\text{-}\{NH(PMes_2)\}_2C_6H_4$ (1.35 g, 2.09 mmol) in CH_2Cl_2 (25 mL) was added dropwise to a solution of $[ZnCl_2(THF)_2]$ (0.59 g, 2.1 mmol) in CH_2Cl_2 (15 mL). The reaction mixture was stirred for 1 h, concentrated in vacuo, and layered with petroleum ether. The product was obtained as white crystals on standing at room temperature. Yield: 1.0 g (62%). Dec: 243−245 °C. ^{1}H NMR ($CDCl_3$, ppm): 8.43 (d, 2H, $^{1}J_{PH} = 461$ Hz, H−P), 6.87 (s, 8H, *m*-H in Mes), 6.59−6.66 (m, 4H in C_6H_4), 3.75 (m, 2H, THF), 2.54 (br, 12H, *o*-CH_3 in Mes), 2.26 (s, 12H, *p*-CH_3 in Mes), 2.2 (br, 12H, *o*-CH_3 in Mes), 1.85 (m, 2H, THF). ^{31}P NMR: −4.5 (d, $^{1}J_{PH} = 461$ Hz). MS (FAB) *m/z* (%): 782.6 $[M^+]$ (5), 745 $[M^+ - Cl]$ (75), 285 $[(Mes_2PHN)^+]$ (65), 269.2 $[(Mes_2P)^+]$ (100), calc for $C_{42}H_{50}N_2P_2ZnCl_2$: M = 781.12.

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Table 5. Crystal Data and Structure Refinement for 1, 2a, 3, and 4

	1	2a	3	4
empirical formula	$C_{42}H_{50}Cl_2N_2P_2Zn\cdot 0.5THF$	$C_{45}H_{56}N_2P_2Zn$	$C_{84}H_{96}N_4P_4Zn_2\cdot 2THF$	$C_{90}H_{108}N_4O_2P_4Zn_2\cdot 4C_7H_8$
M_w	817.10	752.23	1560.48	1900.96
temperature	213(2) K	223(2) K	217(2) K	210(2) K
cryst syst	monoclinic	orthorhombic	triclinic	triclinic
space group	$C2/c$	$Pca2_1$	$P\bar{1}$	$P\bar{1}$
unit cell dimens	$a = 3613.4(5)$ pm $b = 1290.0(2)$ pm $c = 2212.5(3)$ pm $\alpha = 90°$ $\beta = 124.682(2)°$ $\gamma = 90°$	$a = 2322.4(3)$ pm $b = 1077.1(1)$ pm $c = 1602.1(2)$ pm $\alpha = 90°$ $\beta = 90°$ $\gamma = 90°$	$a = 1483.5(5)$ pm $b = 1675.7(6)$ pm $c = 1892.4(7)$ pm $\alpha = 73.296(7)°$ $\beta = 80.234(6)°$ $\gamma = 76.048(7)°$	$a = 1208.8(2)$ pm $b = 1491.0(2)$ pm $c = 1600.2(3)$ pm $\alpha = 93.516(3)°$ $\beta = 102.306(3)°$ $\gamma = 112.238(3)°$
volume	8.48(1) nm^3	4.0076(8) nm^3	4.35(1) nm^3	2.5760(7) nm^3
Z	8	4	2	1
density (calcd)	1.280 g/cm^3	1.247g/cm^3	1.192 g/cm^3	1.225 g/cm^3
absorp coeff	0.814 mm^{-1}	0.726 mm^{-1}	0.673 mm^{-1}	0.580 mm^{-1}
$F(000)$	3440	1600	1656	1012
cryst size	0.40 × 0.20 × 0.10 mm^3	0.40 × 0.20 × 0.10 mm^3	0.30 × 0.20 × 0.05 mm^3	0.30 × 0.10 × 0.10 mm^3
$\theta_{min}/\theta_{max}$	1.37/28.46°	2.08/29.07°	1.13/29.09°	1.83/29.54°
index ranges	$-48 \le h \le 47$ $-17 \le k \le 15$ $-24 \le l \le 28$	$-26 \le h \le 31$ $-14 \le k \le 13$ $-21 \le l \le 16$	$-19 \le h \le 20$ $-22 \le k \le 21$ $-24 \le l \le 24$	$-16 \le h \le 14$ $-19 \le k \le 20$ $-20 \le l \le 21$
no. of reflns collected	26 393	25 734	36 611	23 152
no. of indep reflns	9726 [R(int) = 0.0675]	8963 [R(int) = 0.0845]	20 523 [R(int) = 0.0670]	12 523 [R(int) = 0.0524]
completeness to θ_{max}	90.7%	93.9%	88.0%	87.0%
abs structure param		0.036(17)		
no. of restraints/ params	4/537	1/468	26/911	60/618
goodness-of-fit on F^2	0.916	1.028	0.890	1.138
final R indices [$I > 2\sigma(I)$]	R1 = 0.0457, wR2 = 0.1012	R1 = 0.0627, wR2 = 0.1507	R1 = 0.0712, wR2 = 0.2137	R1 = 0.0860, wR2 = 0.1504
R indices (all data)	R1 = 0.1122, wR2 = 0.1349	R1 = 0.0863, wR2 = 0.1606	R1 = 0.1923, wR2 = 0.2595	R1 = 0.1448, wR2 = 0.1702
largest diff peak and hole	0.454 and −0.303 e Å^{-3}	1.663 and −0.50 e Å^{-3}	01.904 and −0.550 e Å^{-3}	0.641 and −0.425 e Å^{-3}

Preparation of [ZnPr{1-N(PMes$_2$)-2-N(PHMes$_2$)C$_6$H$_4$-κ^2*N,N′*}] (2a). An excess of $ZnPr_2$ (2.63 mL, 1.5 mmol/mL) in petroleum ether was added dropwise to a solution of 1,2-{NH-(PMes$_2$)}$_2$C$_6$H$_4$ (1.75 g, 2.71 mmol) in toluene (25 mL). The reaction mixture was stirred for 1 h and then concentrated. The concentrated solution was layered with THF, and the product was obtained as yellow air-sensitive crystals on standing at room temperature. Yield: 1.31 g (64.5%). Mp: 214−216 °C. ^1H NMR (C_6D_6, ppm): 8.33 (d, 1H, $^1J_{PH} = 459$ Hz, PH), 7.8 (br, 1H, C_6H_4), 7.05−7.09 (m, 1H, C_6H_4), 6.79 (s, 4H, *m*-H in Mes), 6.64−6.67 (m, 1H, C_6H_4), 6.60 (br, 1H, C_6H_4), 6.46 (d, 4H, $^4J_{PH} = 3.8$ Hz, *m*-H in Mes), 2.66 (s, 12H, *p*-CH_3 in Mes), 2.14 (s, 6H, *o*-CH_3 in Mes), 2.05 (br, 12H, *o*-CH_3 in Mes), 1.89 (s, 6H, *o*-CH_3 in Mes), 0.76−0.86 (m, 5H, CH_3CH_2 in ZnPr), −0.53 (br, 2H, CH_2 in ZnPr). ^{31}P NMR: 43.0 (s), −5.2 (d, $^1J_{PH} = 459$ Hz, PH). $^{13}C\{^1H\}$ NMR (C_6D_6, ppm): 152.3 (dd, $^2J_{PC} = 24.3$ Hz, C_6H_4), 144.2 (s, *p*-C in Mes), 142.8 (d, $^2J_{PC} =$ 16.9 Hz, *o*-C in Mes), 141.4 (d, $^1J_{PC} = 16.5$ Hz, *ipso*-C in Mes) 140.6 (d,$^1J_{PC} = 7.8$ Hz, *ipso*-C in Mes), 138.7 (d, $^2J_{PC} = 28.7$ Hz, *o*-C in Mes), 137.7 (s, *p*-C in Mes), 131.8 (d, $^3J_{PC} = 10.3$ Hz, *m*-C in Mes), 131.1 (d, $^3J_{PC} = 1.6$ Hz, *m*-C in Mes), 123.3 (d, $^3J_{PC} = 2.9$ Hz, *m*-C in Mes), 121.5 (s, C_6H_4), 116.8 (d, $^3J_{PC}$ = 36.8 Hz, C_6H_4), 115.6 (s, C_6H_4), 114.3 (d, $^3J_{PC} = 17.4$ Hz, C_6H_4), 22.9 (d, $^3J_{PC} = 16.9$ Hz, *o*-CH_3 in Mes), 22.5 (s, *p*-CH_3 in Mes), 21.7 (s, *p*-CH_3 in Mes), 21.6 (d, $^3J_{PC} = 4.9$ Hz, *o*-CH_3 in Mes), 21.2 (br, CH_3CH_2 in ZnPr), 13.8 (s, CH_2 in ZnPr). MS (FAB) *m/z* (%): 753.3 [M$^+$] (8), 710 [M$^+$ − Pr] (3), 677 [M$^+$ − Pr − 2Me] (35), 645.3 [M$^+$ − ZnPr] (3), 285 [(Mes$_2$PN)$^+$] (100), 269 [(Mes$_2$P)$^+$] (38), calc for $C_{45}H_{56}N_2P_2Zn$: M = 752.23.

Preparation of [ZnEt{1-N(PMes$_2$)-2-N(PHMes$_2$)C$_6$H$_4$-κ^2*N,N′*}] (2b). $ZnEt_2$ (1.5 mL, excess) in 10 mL of hexane was added dropwise to a solution of 1,2-{NH(PMes$_2$)}$_2$C$_6$H$_4$ (0.61 g, 0.947 mmol) in 25 mL of toluene. The reaction mixture was stirred for 1 h and then concentrated. The concentrated solution was layered with THF, and the product was obtained as yellow air-sensitive crystals on standing at room temperature. Yield: 0.43 g (63%). Dec: 231−233 °C. ^1H NMR (C_6D_6, ppm): 8.33 (d, 1H, $^1J_{PH} = 458.5$ Hz, H−P), 7.81 (br, 1H, C_6H_4), 7.07−7.11 (m, 1H, C_6H_4), 6.80 (d, 4H, $^4J_{PH} = 1.4$ Hz, *m*-H in Mes), 6.65−6.69 (m, 1H, C_6H_4), 6.60 (br, 1H, C_6H_4), 6.45 (d, 4H, $^4J_{PH} = 4.4$ Hz, *m*-H in Mes), 2.67 (s, 12H, *p*-CH_3 in Mes), 2.13 (s, 6H, *o*-CH_3 in Mes), 2.05 (br, 12H, *o*-CH_3 in Mes), 1.87 (s, 6H, *o*-CH_3 in Mes), 0.66 (t, 3H, $^3J_{HH} = 7.8$ Hz, CH_3 in ZnEt), −0.51 (q, 2H, $^3J_{HH} = 7.8$ Hz, CH_2 in ZnEt). ^{31}P NMR: 43.1 (s), −5.2 (d, $^1J_{PH} = 458.5$ Hz, PH). $^{13}C\{^1H\}$ NMR (C_4D_8O, ppm): 151.8 (br, C_6H_4), 144.5 (s, *p*-C in Mes), 142.3 (d, $^2J_{PC} = 16.4$ Hz, *o*-C in Mes), 141.4 (d, $^1J_{PC} = 16.9$ Hz, *ipso*-C in Mes), 140.3 (br, *ipso*-C in Mes), 138.5 (d, $^2J_{PC} = 26.7$ Hz, *o*-C in Mes), 137.1 (s, *p*-C in Mes), 131.8 (d, $^3J_{PC} = 11.2$ Hz, *m*-C in Mes), 130.7 (d, $^3J_{PC} = 2.8$ Hz, *m*-C in Mes), 130.3 (s, *m*-C in Mes), 121.6 (s, C_6H_4), 115.4 (d, $^3J_{PC} = 36.8$ Hz, C_6H_4), 114.7 (s, C_6H_4), 113.8 (d, $^3J_{PC} = 17.3$ Hz, C_6H_4), 22.2 (s, *p*-CH_3 in Mes), 21.9 (d, $^3J_{PC}$ = 16.1 Hz, *o*-CH_3 in Mes), 21.1 (s, *p*-CH_3 in Mes), 20.8 (d, $^3J_{PC}$ = 16.1 Hz, *o*-CH_3 in Mes), 20.6 (s, CH_3 in ZnEt), 11.2 (s, CH_2 in ZnEt). MS (FAB) *m/z* (%): 711.2 [M$^+$ − Et] (3), 645.2 [M$^+$ − ZnEt] (2), 375 [M$^+$ − ZnEt − Mes$_2$P] (14), 285 [(Mes$_2$PHN)$^+$] (100), calc for $C_{44}H_{54}N_2P_2Zn$: M = 738.27.

Preparation of [Zn{1-N(PMes$_2$)-2-N(μ-PMes$_2$)C$_6$H$_4$-κ^3*N,N′,P*}]$_2$ (3). ^nBuLi (1.07 mL, 2.23 M in hexane) was added dropwise to a solution of 1,2-{NH(PMes$_2$)}$_2$C$_6$H$_4$ (0.72 g, 1.1 mmol) in THF (25 mL) at −78 °C. The mixture was stirred for 1 h, and 0.25 g of [ZnCl$_2$(THF)$_2$] in THF (15 mL) was added dropwise. The reaction mixture was stirred for 2 h, and the solvent removed in a vacuum. The product was extracted with toluene (25 mL), filtered, and concentrated. THF drops were added to the concentrated solution, and the product was obtained as yellow crystals at 4 °C. Yield: 0.52 g (66%). Dec: 318−320 °C. ^1H NMR (C_4D_8O, ppm): 7.02−7.19 (m, tol), 6.97 (br, 2H, C_6H_4), 6.70 (s, 8H, *m*-H in Mes), 6.66 (br, 2H, C_6H_4), 6.51 (s, 8H, *m*-H in Mes), 6.10 (br, 2H, C_6H_4), 5.45 (br, 2H, C_6H_4), 3.60 (m, THF), 2.30 (s, CH_3 in tol), 2.24 (s, 24H, *o*-CH_3 in Mes), 2.19 (s, 12H, *o*-CH_3 in Mes), 2.14 (s, 24H, *p*-CH_3 in Mes), 2.10 (s, 12H, *o*-CH_3 in Mes), 1.77 (m, THF). ^{31}P NMR (C_4D_8O, ppm, 255 K): 36 (s, 2P, P−Mes), 21.2 (s, 2P, P−Zn).

^{31}P NMR (THF/C_6D_6, ppm, rt): 37.9 (br, s, 3P, P−Mes), 23.2 (s, 1P, P−Zn). ^{13}C{^{1}H} NMR (C_4D_8O, ppm): 150.5 (br, C_6H_4), 142.6 (d, $^2J_{PC}$ = 16.9 Hz, *o*-C in Mes), 141.3 (d, $^2J_{PC}$ = 16.5 Hz, *o*-C in Mes), 140.3 (d, $^1J_{PC}$ = 29.6 Hz, *ipso*-C in Mes), 138.3 (s, *p*-C in Mes), 137.5 (d, $^1J_{PC}$ = 23.2 Hz, *ipso*-C in Mes), 135.5 (s, tol), 135.2 (s, *p*-C in Mes), 130.6 (d, $^3J_{PC}$ = 2.9 Hz, *m*-C in Mes), 129.5 (s, *m*-C in Mes), 129.4 (s, tol), 128.7 (s, tol), 125.8 (s, tol), 120.9 (s, C_6H_4), 119.1 (d, $^3J_{PC}$ = 20.6 Hz, C_6H_4), 114.4 (s, C_6H_4), 113.3 (d, $^3J_{PC}$ = 42.5 Hz, C_6H_4), 68.0 (s, THF), 26.2 (s, THF), 22.7 (d, $^3J_{PC}$ = 17.4 Hz, *o*-CH_3 in Mes), 22.1 (d, $^3J_{PC}$ = 15.7 Hz, *o*-CH_3 in Mes), 21.3 (s, CH_3 in tol), 20.8 (s, *p*-CH_3 in Mes), 20.7 (s, *p*-CH_3 in Mes). MS (FAB) *m*/*z* (%): 1418.1 [M^+] (0.3), 879.6 [$M^+ - 2PMes_2$] (4), 788.7 [$M^+ - 2PMes_2 - NC_6H_4$] (39), 441.3 [$(ZnNC_6H_4NPMes_2)^+$] (7), 375.5 [$(C_6H_4N_2PMes_2)^+$] (22), 285.2 [$(Mes_2PN)^+$] (100), 269.1 [$(PMes_2)^+$] (85), calc for $C_{84}H_{96}N_4P_4Zn_2$: M = 1416.40.

Preparation of [Zn{1-N{PMes$_2$CH$_2$CH(Me)O}-2-N-(PMes$_2$)C$_6$H$_4$)-κ^3*N*,*N′*,*O*}]$_2$ (4). Propylene oxide (0.0139 mL, 0.199 mmol) was added to a solution of **2a** (0.15 g, 0.199 mmol) in toluene (15 mL). The reaction mixture was refluxed for 30 min to obtain a clear solution. The product was obtained as pale yellow air-sensitive crystals on standing at room temperature. Yield: 0.1 g (65%). Dec: 307−310 °C. ^{1}H NMR (C_4D_8O, ppm): 7.07−7.17 (m, tol), 6.82 (s, 8H, *m*-H in Mes), 6.74 (d, $^4J_{PH}$ = 8 Hz, *m*-H in Mes), 6.43 (m, 2H, C_6H_4), 6.19 (m, 4H, C_6H_4), 5.82 (m, 2H, C_6H_4), 3.78 (br, 2H, CHO), 2.52 (m, 4H, CH_2P), 2.28 (s, 24H, *o*-CH_3 in Mes and 12H, CH_3 in tol), 2.20 (s, 24H, *p*-CH_3 in Mes and 12H, *o*-CH_3 in Mes), 2.15 (s, 12H, *o*-CH_3 in Mes), 0.98 (d, $^3J_{HH}$ = 4.4 Hz, 6H, C*H*$_3$CHO). ^{31}P NMR (C_4D_8O, ppm): 16.3 (s, P−Mes), 10.8 (s, P−CH_2). ^{13}C{^{1}H} NMR (C_4D_8O, ppm): 141.6 (d, $^2J_{PC}$ = 9.9 Hz, *o*-C in Mes), 141.2 (d, $^2J_{PC}$ = 9.9 Hz, *o*-C in Mes), 140.8 (d, $^2J_{PC}$ = 16.1 Hz, *o*-C in Mes), 140.6 (s, *p*-C in Mes), 140.4 (d, $^2J_{PC}$ = 16.1 Hz, *o*-C in Mes), 137.8 (s, tol), 137.4 (s, *p*-C in Mes), 137.0 (d, $^1J_{PC}$ = 29.4 Hz, *ipso*-C in Mes), 135.5 (d, $^1J_{PC}$ = 21.9 Hz, *ipso*-C in Mes), 131.2 (d, $^3J_{PC}$ = 9.9 Hz, *m*-C in Mes), 129.6 (d, $^3J_{PC}$ = 4.5 Hz, *m*-C in Mes), 128.6 (s, tol), 127.9 (s, tol), 125.0 (s, tol), 118.5 (d, $^3J_{PC}$ = 10.8 Hz, C_6H_4), 117.9 (s, C_6H_4), 117.2 (s, C_6H_4), 112.0 (d, $^3J_{PC}$ = 26 Hz, C_6H_4), 64.0 (d, $^2J_{PC}$ = 5.0 Hz, CHO), 44.3 (d, $^1J_{PC}$ = 83.9 Hz, *C*H$_2$CHO), 22.2 (d, $^3J_{PC}$ = 4.1 Hz, *C*H$_3$CHO), 21.5 (d, $^3J_{PC}$ = 16.6 Hz, *o*-CH_3 in Mes), 21.3 (d, $^3J_{PC}$ = 17.8 Hz, *o*-CH_3 in Mes), 20.4 (s, CH_3 in tol), 19.9 (s, *p*-CH_3 in Mes), 19.8 (s, *p*-CH_3 in Mes). Assignment was based on ^{1}H−^{13}C-COSY and APT. MS (FAB) *m*/*z* (%): 1442 [$M^+ - CH_3 - NC_6H_4$] (0.2), 1135 [$M^+ - NPMes_2C_6H_4N - Pr$] (1), 765.2 [$(ZnOPr(NPMes_2)_2C_6H_4)^+$] (17), 719.2 [$(ZnCH_2PMes_2NC_6H_4NPMes_2)^+$] (100), 703.3 [$(OPr(NPMes_2)_2C_6H_4)^+$] (18), 285 [$(Mes_2PN)^+$] (41), 269 [$(Mes_2P)^+$] (24), calc for $C_{90}H_{108}N_4O_2P_4Zn_2 \cdot 4C_7H_8$: M = 1900.96.

Data Collection and Structural Refinement of 1−4. Data were collected with a Siemens CCD (SMART) diffractometer (ω-scans, λ(Mo Kα) = 0.71073 Å). Data reduction was performed with SAINT, including SADABS, a program for empirical absorption correction. The structures were solved by direct methods. All non-hydrogen atoms were refined anisotropically; H atoms were mainly calculated on idealized positions. Probably due to loss of some solvent, the structure parameters for compound **3** are of inferior quality and only two THF solvent molecules could unambiguously be identified. Structure pictures were generated with ORTEP for Windows.[34] Crystallographic data can be obtained free of charge via 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; or deposit@ccdc.cam.uk). Any request to the CCDC for material should quote the full literature citation and the references CCDC 271149 (**1**), 271147 (**2a**), 271148 (**3**), and 271150 (**4**).

Supporting Information Available: IR data, elemental analyses, and ^{1}H and ^{13}C NMR spectra. Tables giving X-ray crystallographic data of **1**, **2a**, **3**, and **4**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(34) (a) *SMART*: Area-Detector Software Package; Siemens Industrial Automation, Inc.: Madison, WI, 1993. (b) *SAINT*: Area-Detector Integration Software, Version 6.01; Siemens Industrial Automation, Inc.: Madison, WI, 1999. (c) Sheldrick, G. M. *SADABS*: Program for Scaling and Correction of Area-detector Data; Göttingen, 1997. (d) Sheldrick, G. M. *SHELX97* [includes *SHELXS97*, *SHELXL97*], Programs for Crystal Structure Analysis (Release 97-2); University of Göttingen: Germany, 1997. (e) ORTEP3 for Windows: Farrugia, L. J. *J. Appl. Crystallogr.* **1997**, *30*, 565.