A New Arene-Bridged Diamidophosphine Ligand and Its Coordination Chemistry with Zirconium(IV)

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The arene-bridged dilithium diamidophosphine ligand, [(2,4,6-$Me_3C_6H_2$)NLi-2-(5-MeC_6H_3)]$_2$-PPh, [NPN]*Li_2, was prepared from (2,4,6-$Me_3C_6H_2$)(2-Br-4-MeC_6H_3)NH, ^{n}BuLi, and $PhPCl_2$ in Et_2O and isolated as a dioxane adduct in ∼85% yield. The solid-state structure of [NPN]*$Li_2(THF)_2$ as determined by X-ray diffraction shows both lithiums bridged by the amido nitrogens with one Li ion coordinated to the phosphine donor. The reaction of [NPN]*H_2 and $Zr(NMe_2)_4$ in toluene produced [NPN]*$Zr(NMe_2)_2$ in 90% isolated yield. Addition of excess Me_3SiCl to [NPN]*$Zr(NMe_2)_2$ converts it to [NPN]*$ZrCl_2$ in high yield. The solid-state structure of [NPN]*$ZrCl_2$ as determined by X-ray diffraction shows the Zr center is a distorted trigonal bipyramid with the phosphine and the chloride apical. The *ortho*-Me's on the N-mesityl moiety are inequivalent in both the Li and Zr complexes of [NPN]* by NMR spectroscopy, while in [NPN]*H_2 MesN *ortho*-Me's appear as broad singlets. VT-NMR of [NPN]*H_2 indicated that $\Delta G_{rot}^{\ddagger}$ of $MesC_{ipso}$−N is approximately 15.5 ± 0.3 kcal mol^{-1}. The thermally labile and light-sensitive zirconium dimethyl complex [NPN]*$ZrMe_2$ was prepared from [NPN]*$ZrCl_2$ and MeMgCl in Et_2O in 80% yield.

Introduction

The ability to control the reactivity patterns of a metal complex by appropriate choice of the ancillary ligands is at the core of inorganic chemistry. Examples abound of ligand sets that can facilitate oxidation state changes,[1] allow unusual electronic states,[2] generate chiral environments for asymmetric synthesis,[3] and modulate light absorption for energy transfer.[4] Even though it is not yet possible to predict reaction outcomes on the basis of a particular choice of a ligand set, research into ligand design continues guided by ideas of geometry control, donor atom types, and substituent effects. The recent report of the effect of one methyl group on the ability to completely change the reactivity of a zirconium complex with N_2 and H_2 exemplifies the inability to predict reaction outcomes.[5]

Research in the Fryzuk group has focused on multidentate ligand designs that incorporate different combinations of amido and phosphine donors into chelating arrays. This design strategy takes into account that amido donors generally stabilize high oxidation state, electron-poor metal complexes, while phosphine donors are known to stabilize more electron-rich metal systems. In the activation of molecular nitrogen, such ancillary ligands have enjoyed considerable success due to the fact that highly reducing conditions are generally required for coordination of N_2 to the early transition metals.[6]

While we have reported[7] dinitrogen activation using complexes stabilized with [PNP], [P_2N_2], and [NPN] ligand sets, in each of these cases the linkages have involved N−Si bonds, typically to facilitate ligand synthesis and also to provide reduced basicity of the amido nitrogen donor.[8] Recently, we have discovered that this N−Si linkage is not robust.[9] The hydroboration of the ditantalum dinitrogen complex ([NPN]Ta)$_2$(η^1:η^2-μ-N_2)(μ-H)$_2$ results in cleavage of N_2 and [NPN] decomposition via loss of a phenyl substituent from one amido.[10] The resulting imide-, nitride-bridged ditantalum complex features a newly formed N−Si bond between the [NP] ligand and the bridging imide formed from N_2.

Since ancillary ligand decomposition is a major barrier to the development of a catalytic cycle based on N_2

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functionalization, we sought to develop a more robust diamidophosphine ligand with similar basicity to the N−Si linked [NPN]. For comparison, the pK_a of diphenylamine is 24.95,[11] very similar to that of bis(trimethylsilyl)amine at 25.8.[12] An arene-bridged diamidophosphine with aryl substituents on N and P is therefore likely to provide a similar electronic environment to [NPN], while the aromatic backbone should inhibit the kind of ligand decomposition described above.

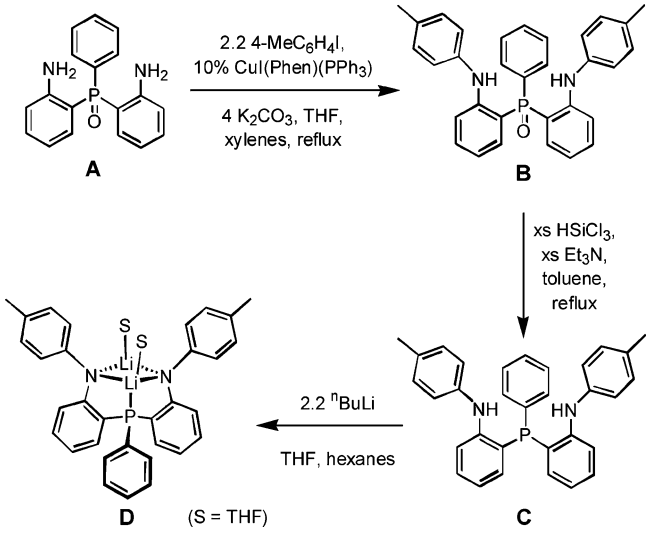
In this work, two main approaches to prepare an arene-bridged diamidophosphine are reported. First, Cu-catalyzed arylation of 2,2′-diaminotriphenylphosphine oxide, (2-$NH_2C_6H_4)_2$PhP═O, followed by phosphine oxide reduction and deprotonation to form [(4-MeC_6H_4)NLi-(2-C_6H_4)]$_2$PPh, [NPN]′Li_2, was investigated, and second, lithiation of (2,4,6-$Me_3C_6H_2$)(2-Br-4-MeC_6H_3)-NH, (Mes)(BrTol)NH, followed by metathesis with Ph-PCl_2 to produce [(2,4,6-$Me_3C_6H_2$)NLi-2-(5-MeC_6H_3)]$_2$-PPh, [NPN]*Li_2, was examined. In addition, the coordination chemistry of this new ligand set with Zr(IV) is included.

Results and Discussion

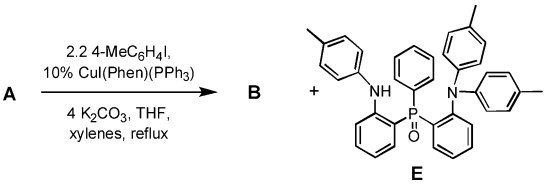
Our first approach to the synthesis of an arene-bridged diamidophosphine was to prepare the phenyl-bridged [NPN]′ ligands (where [NPN]′ = [(4-MeC_6H_4)N-(2-C_6H_4)]$_2$PPh) by Cu-catalyzed arylation of (2-NH_2-$C_6H_4)_2$PhP═O, **A**, which is readily prepared from phenylphosphine ($PhPH_2$) and 2-iodoaniline, in the presence of catalytic Pd(PPh_3)$_4$ and the water-soluble triarylphosphine GUAP-3.[13] Attempts to directly couple 2,2′-diaminotriphenylphosphine to aryliodides were unsuccessful, likely due to binding of the chelating diaminophosphine substrates and products to the copper catalyst. Thus, phosphine oxide **A** was reacted with 2.2 equiv of 4-iodotoluene (Tolyl-I) and catalytic CuI(Phen)(PPh_3) to produce [(4-MeC_6H_4)NH-(2-C_6H_4)]$_2$PhP═O, **B**, in 85% yield by a modification of a literature procedure.[14] Compound **B** was reduced to [NPN]′H_2, **C**, using standard conditions.[15] Finally, addition of 2 equiv of ^{n}BuLi to **C** provided [NPN]′Li_2(THF)$_2$, **D**, in 53% yield (Scheme 1).

[NPN]′Li_2(THF)$_2$ (**D**) displays a $^{31}P\{^1H\}$ NMR spectrum similar to [NPN]Li_2(THF)$_2$ (where NPN = PhP-($CH_2SiMe_2NPh)_2$), previously reported;[16] a quartet is observed at −33.0 ppm due to coupling with ^{7}Li (I = 3/2, J_{PLi} = 41 Hz). As expected, a doublet and a singlet are apparent in the ^{7}Li NMR spectrum of [NPN]′Li_2-(THF)$_2$, indicating that one Li ion is bound to P (−0.35 ppm), while the other Li ion is not closely associated with the phosphine donor (−1.72 ppm). By ^{1}H NMR spectroscopy, two THF molecules are present.

Scheme 1



Scheme 2



There are several drawbacks to the synthesis of **D** shown in Scheme 1. First, the reaction requires four steps from phenylphosphine, which is malodorous to prepare and extremely pyrophoric. Second, the Cu-catalyzed arylation reaction must be refluxed over several days. These conditions promote the formation of the side product [(4-$MeC_6H_4)_2$N(2-C_6H_4)][(4-MeC_6H_4)-NH(2-C_6H_4)]PhP═O, **E**, the product of three Tolyl-I additions to **A**. This product was identified by ^{1}H and $^{31}P\{^1H\}$ NMR spectroscopy and electron impact mass spectrometry (EI-MS), and it must be removed from **B** by extensive chromatography (Scheme 2). Thus, the yield of **B** decreases when the Cu-catalyzed reaction is performed on a multigram scale. It was clear that a new route to arene-bridged diamidophosphines was needed.

As an alternative, we explored diamidophosphine synthesis from (Mes)(BrTol)NH, readily prepared in high yield from (4-MeC_6H_4)(2,4,6-$Me_3C_6H_2$)NH, (Mes)-(Tol)NH,[17] and *N*-bromosuccinimide (NBS). This follows recent reports for the synthesis of related [PNP] ligand sets.[18] (Mes)(BrTol)NH reacts with 2 equiv of ^{n}BuLi over 3 h to form (2-Li-4-MeC_6H_3)(2,4,6-$Me_3C_6H_2$)NLi, **F**, the product of Li/Br exchange. $PhPCl_2$ (0.5 equiv) was added to a solution of intermediate **F** to produce [(2,4,6-$Me_3C_6H_2$)NLi-2-(5-MeC_6H_3)]$_2$PPh, **1**, by a metathesis reaction. The dioxane adduct of **1** was isolated in up to 85% yield (Scheme 3). The tmeda adduct of **F**, (2-Li-4-MeC_6H_3)(2,4,6-$Me_3C_6H_2$)NLi·($Me_2NCH_2CH_2NMe_2)_2$, was also isolated and was characterized by ^{1}H NMR spectroscopy. The isolation of intermediate **F** and subsequent reaction with $PhPCl_2$ (0.5 equiv) were not found

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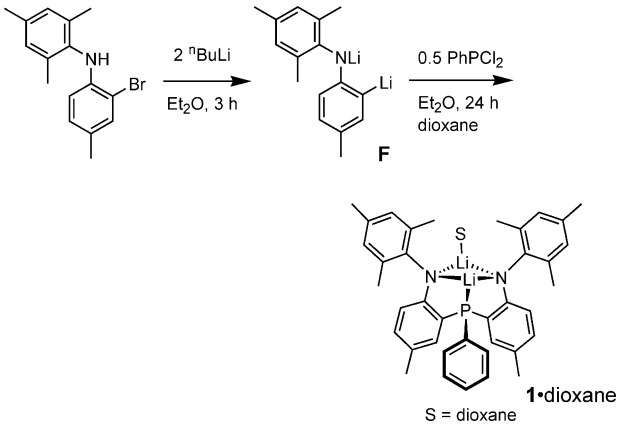
Scheme 3



to increase the yield of [NPN]*Li_2, in comparison to the one-pot reaction described above.

Like other NPN lithium salts,[16,19] the $^{31}P\{^1H\}$ NMR spectrum of **1**·dioxane shows a quartet at −35.2 ppm (J_{PLi} = 40 Hz), and the ^7Li NMR spectrum shows a doublet at −0.07 ppm and a singlet at −1.97 ppm. The ^1H NMR spectrum of **1**·dioxane is notable in that *ortho*-Me and *meta*-CH protons of the N-mesityl unit are inequivalent, due to restricted rotation about the N−C bond of these groups on the NMR time scale at room temperature.

Crystals of **1**·2THF suitable for X-ray analysis were grown by slow evaporation of a solution of **1**·dioxane in C_6D_6 and THF. The solid-state molecular structure of **1**·2THF (Figure 1) determined by single-crystal X-ray diffraction shows two distinct Li environments: Li1 is coordinated to N1, N2, and P1, and O1 of one coordinated THF, while Li2 is coordinated to N1 and N2, and O2 of the second coordinated THF. Although spectroscopic and X-ray diffraction techniques confirmed the identity of **1**·2THF, microanalysis of this compound has repeatedly shown it to be low in carbon, likely due to the extreme air- and moisture-sensitivity of this material.

The reaction of the dilithium salt **1**·dioxane with $ZrCl_4(THF)_2$ under various conditions led to the formation of multiple products by $^{31}P\{^1H\}$ NMR spectroscopy. Thus, the preparation of zirconium complexes of [NPN]* from the protonated ligand precursor was investigated. To prepare [NPN]*H_2 (**2**), Me_3NHCl was stirred with [NPN]*Li_2(dioxane) in THF. The $^{31}P\{^1H\}$ NMR spectrum of **2** in C_6D_6 solution has a singlet at −31.4 ppm, and the ^1H NMR spectrum at room temperature consists of broad singlets for the *ortho*-Me's and *meta*-CH's on the N-mesityl substituents, indicating hindered rotation about the N−C bond of the bulky mesityl group. In the variable-temperature ^1H NMR experiment, coalescence of the broad Me singlets was observed at 320 K; thus, $\Delta G^{\ddagger}_{rot}$ was calculated to be 15.5 ± 0.3 kcal mol^{-1}.[20]

Zirconium complexes of [NPN]* were synthesized from [NPN]*H_2 and $Zr(NMe_2)_4$ in toluene. The reaction was complete in 2 h at room temperature, and [NPN]*$Zr(NMe_2)_2$ (**3**) was formed as a yellow powder in high yield (Scheme 3). The $^{31}P\{^1H\}$ NMR spectrum of **3** in C_6D_6 has a singlet at −11.5 ppm, and the ^1H NMR spectrum has four singlets for the [NPN]* Me's, indicating that two *ortho*-Me's of the N-mesityl substituents are not exchanging on the NMR time scale. There are two NMe_2 resonances at 3.06 and 2.31 ppm, corresponding to two different NMe environments. We propose that Zr is a five-coordinate trigonal bipyramid, with one NMe_2 apical and the other equatorial, with free rotation about each of the Zr−NMe_2 bonds. The ^1H NMR spectrum shows the complex has a mirror plane of symmetry in solution. Addition of THF, pyridine, or PMe_3 to [NPN]*$Zr(NMe_2)_2$ in benzene produces no color change or shift in the resonance in the $^{31}P\{^1H\}$ NMR spectrum. The ^1H and $^{31}P\{^1H\}$ NMR spectra of **3** are similar to those of [$PhP(CH_2SiMe_2NAr)_2$]$Zr(NMe_2)_2$.[21]

[NPN]*$ZrCl_2$ (**4**) was readily synthesized by reaction of excess Me_3SiCl with **3** in toluene and isolated in 89% yield as a bright yellow powder (Scheme 4). A singlet at −2.8 ppm was observed in the $^{31}P\{^1H\}$ NMR spec-

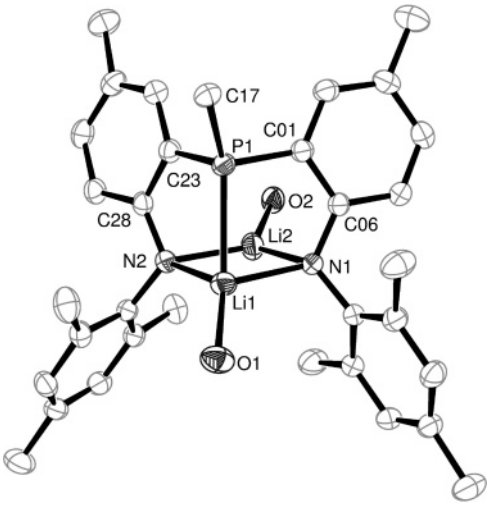
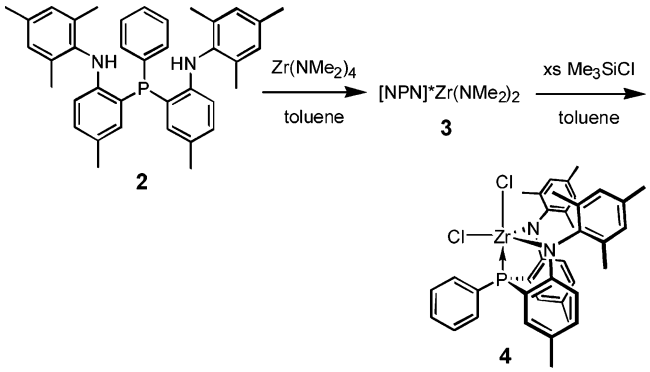


Figure 1. ORTEP drawing of the solid-state structure of **1**·2THF (ellipsoids drawn at the 50% probability level). All hydrogen atoms and carbon atoms of THF and phenyl (except ipso C) have been omitted for clarity. Selected bond lengths (Å) and angles (deg): P1−Li1 2.510(3), N1−Li1 2.078(3), N1−Li2 2.046(4), Li1...Li2 2.518(4), O1−Li1 1.908(3), O2−Li2 1.932(3), N2−Li2 2.051(3), N2−Li1 2.076(3), P1−Li1−Li2 77.01(11), N1−Li2−N2 105.76(15), O1−Li1−Li2 144.07(18), C06−N1−C08 116.60(14), C01−P1−C23 105.40(8), C23−P1−C17 103.18(8), C01−P1−C17 105.62(8).

Scheme 4



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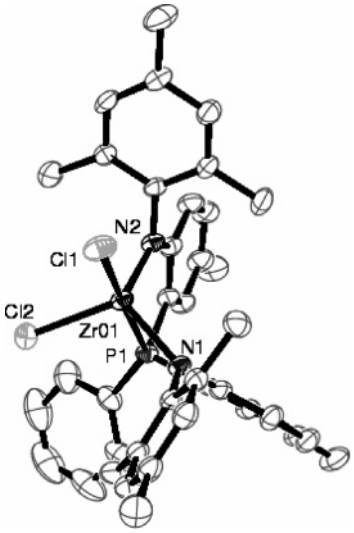


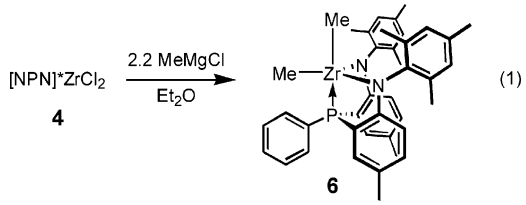
Figure 2. ORTEP drawing of the solid-state structure of **4** (ellipsoids at 50% probability). Selected bond lengths (Å) and angles (deg): Zr1−N1 2.060(2), Zr1−N2 2.072(2), Zr1−P1 2.7229(8), Zr1−Cl1 2.4279(8), Zr1−Cl2 2.4099(8), N1−Zr1−N2 113.96(9), N1−Zr1−P1 72.73(7), N1−Zr1−Cl1 106.25(7), Cl1−Zr1−Cl2 96.23(3), P1−Zr1−Cl1 178.63(3), P1−Zr1−Cl2 85.02(3).

trum in C_6D_6. ^{1}H NMR spectroscopy shows that the *ortho*-Me and *meta* C−H groups of MesN are inequivalent, as with **1** and **3**.

Crystals of **4** were grown from a concentrated benzene solution and analyzed by single-crystal X-ray diffraction. The ORTEP drawing is shown in Figure 2. In the solid state, the stereochemistry around Zr is distorted trigonal bipyramidal with Cl1 and P1 apical, and N1, N2, and Cl2 bent below the 90° plane (by 16°, 6°, and 19°, respectively). The [NPN]* ligand coordinates to Zr facially, and the two chlorides are cis to each other. The Zr−N (average 2.066(5) Å), Zr−Cl (2.419(2) Å), and Zr−P (2.7229(8) Å) bond lengths are not atypical.

The THF adduct of [NPN]*$ZrCl_2$ (**4**) was readily prepared by addition of THF to solutions of **4** in benzene or toluene to generate bright red-orange [NPN]*$ZrCl_2$(THF), **5**; diagnostic of its formation was the downfield shift in the ^{31}P{^{1}H} NMR resonance from −2.8 found for **4** to 2.7 ppm for **5**.

By addition of methylmagnesium chloride to an ethereal suspension of **4** at −35 °C, [NPN]*$ZrMe_2$ (**6**) was prepared in high yield as a highly photo- and thermosensitive yellow powder (eq 1). It is characterized by a singlet at −14.1 ppm in the ^{31}P{^{1}H} NMR spectrum. In the ^{1}H NMR spectrum two distinct zirconium-methyl resonances are observed: a doublet at 0.93 ppm (J_{PH} = 5 Hz) and a singlet at −0.11 ppm. There are four singlets for the [NPN]* methyl substituents. The aryl region is consistent with **6** having C_s symmetry. The structural assignment of **6** is supported by ^{13}C{^{1}H} NMR spectroscopy, which shows the expected peaks for [NPN]* and two resonances for the zirconium methyls: two doublets at 45.1 ppm (J_{CP} = 6 Hz) and 41.8 (J_{CP} = 29 Hz) correspond to Me's trans and cis disposed to P, respectively, in analogy with that described elsewhere.[21] Efforts to confirm this using NOEDIFF experiments were inconclusive. However, HMQC showed that the singlet at −0.11 ppm in the ^{1}H NMR spectrum of **6** is correlated to the doublet at 41.8 ppm (J_{CP} = 29 Hz) in the ^{13}C{^{1}H} NMR spectrum. Similarly, the doublet at 0.93 ppm in the ^{1}H NMR spectrum is correlated to the doublet at 45.1 ppm (J_{CP} = 6 Hz) in the ^{13}C{^{1}H} NMR spectrum. Crystals suitable for X-ray diffraction have not yet been obtained, due in part to the instability of the complex.



Conclusions

A synthetic pathway to arene-bridged diamidophosphine ligands has been developed from a readily prepared diarylamine and commercially available dichlorophenylphosphine. This route provides [NPN]*Li_2 as the dioxane adduct in three steps in high yield in multigram quantities and avoids the use of $PhPH_2$, which is both expensive and malodorous. Zirconium complexes of [NPN]* were prepared via a protonolysis route from $Zr(NMe_2)_4$. Single-crystal X-ray diffraction indicates that [NPN]*$ZrCl_2$ is a monomeric, distorted trigonal bipyramidal complex in solution and the solid state. We are currently investigating the ability of these organometallic compounds of [NPN]*Zr to undergo migratory insertion processes as well as act as polymerization catalysts; in addition, reduction of [NPN]*$ZrCl_2$ under N_2 is a current priority in our laboratory.

Experimental Section

General Considerations. Unless otherwise stated all manipulations were performed under an atmosphere of dry, oxygen-free dinitrogen or argon by means of standard Schlenk or glovebox techniques (Vacuum atmospheres HE-553-2 glovebox equipped with a MO-40-2H purification system and a −40 °C freezer). Argon and nitrogen were dried and deoxygenated by passing the gases through a column containing molecular sieves and MnO. Hexanes, toluene, tetrahydrofuran, pentane, and diethyl ether were purchased anhydrous from Aldrich, sparged with nitrogen, and passed through columns containing activated alumina and Ridox catalyst. Dioxane was dried by refluxing over sodium-benzophenone ketyl and distilled. Deuterated toluene and benzene were dried by refluxing over sodium/potassium alloy under partial pressure, trap-to-trap distilled, and freeze−pump−thaw degassed three times. ^{1}H, ^{31}P{^{1}H}, and ^{13}C{^{1}H} NMR spectra were recorded on a Bruker AV-300, a Bruker AV-400, or a Bruker AMX-500, operating at 300.1, 400.0, and 500.1 MHz for ^{1}H spectra, respectively. ^{7}Li NMR spectra were recorded on the AV-400 or AMX-500. ^{1}H NMR spectra were referenced to residual protons in the deuterated solvent: C_6D_6 (7.16 ppm), $CDCl_3$ (7.24 ppm), C_7D_8 (2.09 ppm), or d_8-THF (3.58 ppm). ^{31}P{^{1}H} NMR spectra were referenced to external $P(OMe)_3$ (141.0 ppm with respect to 85% H_3PO_4 at 0.0 ppm). ^{13}C{^{1}H} spectra are referenced to residual solvent: C_6D_6 (128.0 ppm), $CDCl_3$ (77.23 ppm), or d_8-THF (67.4 ppm). ^{7}Li NMR spectra were referenced to external LiCl in D_2O/H_2O at 0.0 ppm. Chemical shifts (δ) are listed as ppm, and coupling constants are in Hz. Me_3SiCl and $PhPCl_2$ (Aldrich) were distilled prior to use. $(2\text{-}NH_2C_6H_4)_2PPh$,[13] $Zr(NMe_2)_4$,[22] CuI(Phen)(PPh_3),[14] and (Mes)(Tol)NH[17] were pre-

(22) Diamond, G. M.; Jordan, R. F.; Petersen, J. L. *J. Am. Chem. Soc.* **1996**, *118*, 8024.

Table 1. X-ray Diffraction Crystal Data and Structure Refinement for Li_2[NPN]*$(THF)_2$ (1·2THF) and [NPN]*$ZrCl_2$ (4)

	1·2THF	4
empirical formula	$C_{46}H_{55}Li_2O_2P$	$C_{53}H_{54}Cl_2N_2PZr$
cryst description	colorless tablet	yellow needle
cryst size (mm^3)	0.30 × 0.25 × 0.10	0.35 × 0.35 × 0.20
fw	712.77	912
cryst syst	monoclinic	monoclinic
space group	*P*2(1)/*n*	*C*2/*c*
a, b, c (Å)	12.0195(11), 24.292(2), 14.2557(11)	44.638(2), 10.8958(5), 19.4505(9)
β (deg)	102.308(4)	94.334(2)
V ($Å^3$)	4066.7(6)	9433.0(8)
Z	4	8
D_{calcd} (g cm^{-3})	1.164	1.166
μ(Mo Kα) (mm^{-1})	0.106	0.411
F(000)	1528	3416
θ range (deg)	1.68−27.88	1.83−27.98
limiting indices	$-15 \le h \le 15$, $-31 \le k \le 31$, $-18 \le l \le 17$	$-58 \le h \le 58$, $-12 \le k \le 14$, $-25 \le l \le 25$
no. of reflns collected	54955	95473
no. of indep reflns	9577	11331
no. of params	486	541
ρ_{max}, ρ_{min}, e $Å^{-3}$	0.720, −0.472	0.920, −0.661
R1[a]	0.0510	0.0505
wR2[a]	0.1411	0.1379
GOOF on F^2	1.044	1.163

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$, 2$\sigma$ data; $wR2 = [\sum(w(F_o^2 - F_c^2)^2)/\sum w(F_o^2)^2]^{1/2}$ all data.

pared by literature methods. All other compounds were purchased from commercial suppliers and used as received. Mass spectrometry (EI-MS) and microanalyses (C, H, N) were performed at the Department of Chemistry at the University of British Columbia.

Preparation of Compounds. [(4-MeC$_6$H$_4$)NH(2-C$_6$H$_4$)]$_2$PhP=O (B). In air, (2-$NH_2C_6H_4)_2$PPh (1.0 g, 3.4 mmol) was dissolved in hexanes (30 mL) and acetone (5 mL). H_2O_2 (30% w/v, 0.5 mL) was added dropwise to the stirring solution. Solvent was removed, and the pale brown residue was extracted from CH_2Cl_2/water (3 × 50 mL). The organic layer was dried over Na_2SO_4, filtered, and concentrated *in vacuo*. Compound **A** was recrystallized from acetone/EtOAc. In air, the beige solids were dissolved in xylenes (30 mL) and THF (10 mL), and K_2CO_3 (2.0 g, 14.5 mmol), 4-iodotoluene (1.64 g, 7.5 mmol), and CuI(Phen)(PPh_3) (0.220 g, 0.35 mmol) were added. The solution was refluxed for 4 days at about 120 °C. The solvents were removed, and **B** was isolated by silica gel chromatography (9:1 petroleum ether/EtOAc) as a beige powder (1.42 g, 85%).

^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.52 (bs, 2H, N*H*), 7.67 (dd, 2H, J_{HH} = 8 Hz, J_{HP} = 7 Hz), 7.51 (t, 1H, 7 Hz), 7.44 (m, 2H), 7.29 (m, 4H), 7.03 (d, 4H, 8 Hz), 6.97 (d, 4H, 8 Hz), 6.86 (dd, 2H, J_{HH} = 8 Hz, J_{HP} = 7 Hz) and 6.68 (t, 2H, 7 Hz) (Ar*H*), 2.26 (s, 6H, CH_3). ^{31}P{^{1}H} NMR ($CDCl_3$, 121 MHz): δ 42.4 (s). ^{13}C{^{1}H} NMR ($CDCl_3$, 75 MHz): δ 150.9 (d, J_{CP} = 5 Hz), 139.0, 133.8, 133.7, 133.6 (d, J_{CP} = 2 Hz), 132.4, 132.3, 132.2, 129.9, 128.7 (d, J_{CP} = 23 Hz), 121.7, 118.0 (d, J_{CP} = 13 Hz), 115.2 (d, J_{CP} = 8 Hz), and 113.6 (Ar*C*), 20.9 (*C*H_3). EI-MS (*m/z*): 488 (100, M^+), 305 (50, M^+ − TolNHPh), 183 (40, [TolNHPh]$^+$).

[(4-MeC$_6$H$_4$)$_2$N(2-C$_6$H$_4$)][(4-MeC$_6$H$_4$)NH(2-C$_6$H$_4$)]PhP=O (E). Compound **E** was obtained as an impurity when the above reaction was repeated with >5 g of (2-$NH_2C_6H_4)_2$PPh. The off-white product was purified by silica gel chromatography (4:1 petroleum ether/EtOAc) and recrystallized from EtOH/H_2O.

^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.41 (m, 4H), 7.31−7.07 (m, 8H), 7.03 (d, 2H, 8 Hz), 6.94 (d, 2H, 8 Hz), 6.71 (bd, 8H), and 6.54 (t, 1H, 7 Hz) (Ar*H*), 2.27 (s, 3H) and 2.12 (s, 6H) (CH_3). ^{31}P{^{1}H} NMR ($CDCl_3$, 121 MHz): δ 34.1 (s). ^{13}C{^{1}H} NMR ($CDCl_3$, 75 MHz): δ 152.2 (d, J_{CP} = 3 Hz), 149.8 (d, 4 Hz), 145.8, 139.3, 135.4 (d, 11 Hz), 133.5 (d, 2 Hz), 133.2 (d, 11 Hz), 132.6 (d, 3 Hz), 132.5, 132.4 (d, 2 Hz), 132.0 (d, 10 Hz), 131.4, 131.2 (d, 6 Hz), 131.1 (d, 3 Hz), 130.9, 129.7, 129.2, 128.1 (d, 12 Hz), 124.7 (d, 13 Hz), 123.8, 120.4, 117.4 (d, 7 Hz), 116.4 and 115.0 (Ar*C*), 20.9 and 20.8 (*C*H_3). EI-MS (*m/z*): 578 (100, M^+). Anal. Calcd for $C_{39}H_{35}N_2OP$: C, 80.95; H, 6.10; N, 4.84. Found: C, 80.63; H, 6.22; N, 5.24.

[(4-MeC$_6$H$_4$)NH(2-C$_6$H$_4$)]$_2$PhP (C). Toluene (30 mL), trichlorosilane (1.2 g, 8.9 mmol), and triethylamine (0.62 g, 6.1 mmol) were added to **B** (1.0 g, 2.1 mmol) under N_2 in a long Schlenk tube. The solution was refluxed overnight. The white suspension was cooled, degassed H_2O (3 mL) was added, and the volatiles were removed. The solids were triturated with toluene (25 mL), and the suspension was filtered through Celite. The solution was concentrated, and a white solid was obtained (1.07 g, 2.3 mmol, 92%).

^{1}H NMR (C_6D_6, 300 MHz): δ 7.48 (bd, 2H), 7.29 (m, 4H), 7.04 (m, 5H), 6.82 (d, 4H, 8 Hz), 6.76 (d, 4H, 8 Hz), and 6.72 (m, 2H) (Ar*H*), 6.36 (bs, 2H, N*H*), 2.06 (s, 6H, CH_3). ^{31}P{^{1}H} NMR (C_6D_6, 121 MHz): δ −30.9 (bs). ^{13}C{^{1}H} NMR (C_6D_6, 75 MHz): δ 148.5 (bs), 140.4, 135.2 (bs), 134.6, 134.3 (bs), 131.5, 130.8, 130.1, 129.2, 129.1, 122.5, 121.2, 120.5, and 116.6 (Ar*C*), 20.7 (*C*H_3).

[(4-MeC$_6$H$_4$)NLi(2-C$_6$H$_4$)]$_2$PhP·2THF (D). ^{n}BuLi (1.6 M in hexanes, 1.1 mL, 1.75 mmol) was added dropwise to a solution of **C** (0.37 g, 0.78 mmol) in hexanes (10 mL) and THF (1 mL) at −35 °C. A yellow precipitate formed overnight and was isolated on a frit, washed with pentane (3 × 1 mL), and dried. Compound **D** was recrystallized from THF/toluene layered with pentane (0.26 g, 53%).

^{1}H NMR (C_6D_6, 500 MHz): δ 7.81 (bt, 2H, 6 Hz, Ar*H*), 7.74 (t, 2H, 7 Hz, ArH), 7.66 (t, 2H, 7 Hz, ArH), 7.38 (d, 4H, 8 Hz, ArH), 7.13 (m, 8H, ArH), 7.02 (t, 1H, 7 Hz, ArH), 6.67 (t, 2H, 7 Hz, ArH), 2.96 (bs, 8H, THF), 2.27 (s, 6H, Me), 0.87 (bs, 8H, THF). ^{31}P{^{1}H} NMR (C_6D_6, 202 MHz): δ −33.0 (q, J_{PLi} = 41 Hz). ^{7}Li NMR (C_6D_6, 194 MHz): δ −0.35 (d, 1Li, J_{LiP} = 41 Hz), −1.72 (s, 1Li).

(2,4,6-Me$_3$C$_6$H$_2$)(2-Br-4-MeC$_6$H$_3$)NH, (Mes)(BrTol)NH. In air, *N*-bromosuccinimide (3.0 g, 16.9 mmol) was added portionwise to a stirring solution of (Mes)(Tol)NH (3.8 g, 16.9 mmol) in CH_3CN (100 mL) at 0 °C over 30 min. The solution was warmed to room temperature, and a saturated solution of $NaHSO_3$ (5 mL) was added. The solution was evaporated to dryness. The beige solids were purified by flash column chromatography on silica gel (9:1 petroleum ether/ethyl acetate). The first fraction was collected and concentrated to yield beige crystals, which were isolated by filtration, washed with petroleum ether (2 × 10 mL), and dried (4.9 g, 96%).

^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.33 (s, 1H, *m*-Tol*H*), 6.96 (s, 2H, *m*-Mes*H*), 6.83 and 6.07 (d, 1H, 8 Hz, *o*-, *m*-Tol*H*), 5.51 (bs, 1H, N*H*), 2.33 (s, 3H, CH_3), 2.23 (s, 3H, CH_3), 2.17 (s, 6H, *o*-CH_3). ^{13}C{^{1}H} NMR (C_6D_6, 75 MHz): δ 141.5, 136.5, 136.0, 135.5, 132.9, 129.4, 129.1, 128.1, 112.6, and 109.4 (Ar*C*), 21.1, 20.2, and 18.3 (*C*H_3). EI-MS (*m/z*): 303 [100, M^+]. Anal. Calcd for $C_{16}H_{18}N$: C, 63.17; H, 5.96; N, 4.60. Found: C, 62.81; H, 5.99; N, 4.72.

(2,4,6-Me$_3$C$_6$H$_2$)(2-Li-4-Me-C$_6$H$_3$)NLi·2(tmeda) (F·2tmeda). A solution of (Mes)(BrTol)NH (0.79 g, 2.59 mmol) and tmeda (0.80 mL, 5.30 mmol) in Et_2O (5 mL) was cooled to −35 °C, and 2.1 equiv of ^{n}BuLi (3.4 mL, 1.6 M in hexanes, 5.44 mmol) was added dropwise with stirring. A light yellow precipitate formed immediately and was isolated and dried (0.68 g, 1.44 mmol, 56%).

^{1}H NMR (THF-d_8, 300 MHz): δ 6.93 (d, 1H, 2 Hz, ArH), 6.74 (s, 2H, ArH), 6.38 (dd, 1H, 8 Hz, 2 Hz, ArH), 5.54 (d, 1H, 8 Hz, ArH), 2.31 (s, 4H, tmeda), 2.17 (s, 3H, CH_3), 2.15 (s, 12H, tmeda), 2.02 (s, 3H, CH_3), 2.00 (s, 6H, CH_3). ^{13}C{^{1}H} NMR (THF-d_8, 75 MHz): δ 153.8, 152.1, 133.5, 132.2, 129.4, 129.3, 128.4, 116.4, 113.3, and 111.5 (Ar*C*), 58.8 and 46.2 (tmeda), 21.0, 20.0, and 18.9 (CH_3).

[NPN]*Li$_2$(dioxane) (1·dioxane). To a solution of (Mes)(BrTol)NH (4.84 g, 15.9 mmol) in Et_2O (100 mL) at −35 °C was added ^{n}BuLi (1.55 M in hexanes, 20.5 mL, 31.8 mmol) dropwise over 1 h. The clear yellow solution was warmed to room temperature and stirred for 3 h. The solution was chilled (−35 °C), and $PhPCl_2$ (1.40 g, 7.8 mmol) in Et_2O (10 mL) was added dropwise over 2 h. The orange solution was warmed slowly to room temperature and stirred for 24 h. The solvent was removed, and hexanes (30 mL) and 1,4-dioxane (5 mL) were added to the orange foam. A yellow precipitate formed, which was collected on a frit and washed with hexanes. The dark orange filtrate was concentrated and chilled to yield additional yellow precipitate. The combined isolated solids were dissolved in toluene (50 mL) and THF (0.5 mL), filtered through Celite, and taken to dryness. The yellow powder was recrystallized from toluene/hexanes and dried *in vacuo* (4.4 g, 85% isolated yield based on $PhPCl_2$). NMR spectroscopy was facilitated by the addition of a drop of THF to the suspension of **1**·dioxane in C_6D_6. Although crystals and powders of **1**·dioxane decompose at room temperature over a period of a few days, **1**·dioxane can be stored in crystalline form at −35 °C for months. Elemental analyses of **1**·dioxane were hampered by its sensitivity to moist air; despite many attempts, results that were low in carbon were found.

^{1}H NMR (C_6D_6, 300 MHz): δ 7.81 (t, 2H, $J_{HP} = J_{HH} = 7$ Hz), 7.72 (bd, 2H, 3 Hz), 7.19 (t, 2H, 7 Hz), 7.02 (t, 1H, 8 Hz), 6.97 (s, 2H), 6.87 (s, 2H), 6.85 (d, 2H, 8 Hz), and 6.52 (dd, 2H, 8 Hz) (Ar*H*), 3.36 (s, 8H, $C_4H_8O_2$) 2.35 (s, 6H), 2.33 (s, 6H), 2.28 (s, 6H), and 2.16 (s, 6H) (CH_3). ^{31}P{^{1}H} NMR (C_6D_6, 121 MHz): δ −35.2 (q, $J_{PLi} = 40$ Hz). ^{7}Li NMR (C_6D_6, 155 MHz): δ −0.07 (d, 1Li, $J_{PLi} = 40$ Hz), −1.97 (s, 1Li). ^{13}C{^{1}H} NMR (C_6D_6, 75 MHz): δ 162.1 ($J_{CP} = 28$ Hz), 152.0, 140.2, 134.9 ($J_{CP} = 3$ Hz), 133.8, 132.3 ($J_{CP} = 14$ Hz), 132.2, 132.1, 131.8, 130.8, 129.0, 128.8, 126.8, 122.9, 120.9 ($J_{CP} = 12$ Hz), and 117.9 ($J_{CP} = 5$ Hz) (Ar*C*), 67.1 (C_4H_8O), 20.9, 20.7, 20.4, and 20.2 (*C*H_3). Anal. Calcd for $C_{46}H_{55}N_2Li_2O_2P$: C, 77.51; H, 7.78; N, 3.93. Found: C, 74.75; H, 7.59; N, 4.02.

[NPN]*H$_2$ (2). Trimethylammonium chloride (0.319 g, 3.3 mmol) was added all at once to a stirring solution of **1**·dioxane (1.06 g, 1.6 mmol) in THF (15 mL). After 1 h, solvent was removed from the beige suspension and toluene was added (20 mL). The toluene suspension was filtered through Celite and the filtrate taken to dryness. The solids were washed with pentane and dried to yield a white powder (0.87 g, 97%).

^{1}H NMR (C_6D_6, 300 MHz, 300 K): δ 7.68 (dd, 2H, $J_{PH} = 7$ Hz, $J_{HH} = 7$ Hz, Ar*H*), 7.29 (d, 2H, $J_{PH} = 7$ Hz, Ar*H*), 7.12 (d, 6 Hz, 4H, Ar*H*), 7.02 (t, 1H, 8 Hz, *p*-PhP), 6.88 (d, 2H, 7 Hz, Ar*H*), 6.78 (bs, 2H, *m*-Mes*H*), 6.74 (bs, 2H, *m*-Mes*H*), 6.38 (dd, 2H, $J_{PH} = 5$ Hz, $J_{HH} = 9$ Hz, Ar*H*), 5.98 (d, 2H, $J_{PH} = 5$ Hz, N*H*), 2.12 (s, 6H, CH_3), 2.04 (bs, 6H, *o*-CH_3), 1.98 (s, 6H, CH_3), 1.90 (bs, 6H, *o*-CH_3). ^{1}H NMR ($C_6D_5CD_3$, 500 MHz, 273 K): δ 7.63 (t, 2H, 7 Hz), 7.26 (d, 2H, 7 Hz), 7.10 (m, 3H), 6.84 (d, 2H, 7 Hz), 6.75 (s, 2H), 6.69 (s, 2H), 6.35 (dd, 2H, $J_{PH} = 5$ Hz, $J_{HH} = 9$ Hz), 5.91 (d, 2H, 5 Hz, N*H*), 2.16 (s, 6H), 2.08 (s, 6H), 2.01 (s, 6H), 1.93 (s, 6H). ^{1}H NMR ($C_6D_5CD_3$, 300 MHz, 370 K): δ 7.59 (t, 2H, 8 Hz), 7.12 (m, 4H), 6.95 (m, 1H), 6.82 (d, 2H, 8 Hz), 6.73 (s, 4H), 6.23 (dd, 2H, $J_{PH} = 5$ Hz, $J_{HH} = 9$ Hz), 5.88 (bd, 2H, $J_{PH} = 5$ Hz), 2.12 (s, 6H), 2.01 (s, 6H), 1.98 (s, 12H, *o*-CH_3). ^{31}P{^{1}H} NMR (C_6D_6, 121 MHz, 300K): δ −31.4 (s). ^{13}C{^{1}H} NMR (C_6D_6, 75 MHz, 300 K): δ 147.4 ($J_{CP} = 16$ Hz, Ar*C*), 136.2 (Ar*C*), 135.4 and 135.2 (bs, *o*-, *m*-Mes*C*), 134.8, 134.7, 134.4, 134.2, 131.5, 129.3, 128.8, 128.7 ($J_{CP} = 4$ Hz), 117.9 (d, $J_{CP} = 7$ Hz), and 112.5 ($J_{CP} = 3$ Hz) (Ar*C*), 20.6 (*C*H_3), 20.1 (*C*H_3), 18.0 (bs, *o*-*C*H_3), 17.7 (bs, *o*-*C*H_3). EI-MS (*m/z*): 556 (20, M^+), 541 (100, M^+ − Me). Anal. Calcd for $C_{38}H_{41}N_2P$: C, 81.98; H, 7.42; N, 5.03. Found: C, 82.04; H, 7.46; N, 4.87.

[NPN]*Zr(NMe$_2$)$_2$ (3). $Zr(NMe_2)_4$ (0.58 g, 2.2 mmol) and **2** (1.20 g, 2.2 mmol) were mixed together, and toluene (15 mL) was added. The lemon yellow solution was stirred for 2 h and the solvent removed to yield a yellow residue. Upon addition of pentanes (5 mL), a light yellow precipitate formed, which was isolated on a frit and dried (1.4 g, 90%).

^{1}H NMR (C_6D_6, 300 MHz): δ 7.60 (t, 2H, 8 Hz, *o*-PPh), 7.52 (d, 2H, 7 Hz, *p*-PTol), 7.11 (m, 3H, 7 Hz, *m*-, *p*-PPh), 7.02 (s, 2H, *m*-Mes), 6.97 (s, 2H, *m*-Mes), 6.93 (d, 2H, 9 Hz, *m*-PTol), 6.19 (dd, 2H, 8 Hz, *o*-PTol), 3.06 (s, 6H, N(CH_3)$_2$), 2.42 (s, 6H), 2.32 (s, 6H), 2.31 (s, 6H), 2.25 (s, 6H), and 2.08 (s, 6H) (ArCH_3 and N(CH_3)$_2$). ^{31}P{^{1}H} NMR (C_6D_6, 121 MHz): δ −11.5. ^{13}C-{^{1}H} NMR (C_6D_6, 75 MHz): δ 161.5 ($J_{CP} = 31$ Hz), 145.2, 144.6, 137.2, 136.4, 135.0, 134.7, 134.3, 133.3, 133.1, 130.3, 130.2, 118.0, 117.6, 115.1, and 115.0 (Ar*C*), 43.6 and 43.5 (N(*C*H_3)$_2$), 21.0, 20.4, 19.3, and 19.2 (*C*H_3). EI-MS (*m/z*): 732 (<1, M^+), 688 (30, M^+ − NMe_2), 556 (30, M^+ − $Zr(NMe_2)_2$), 541 (100, M^+ − $Zr(NMe_2)_2$, − Me). Anal. Calcd for $C_{42}H_{45}N_4PZr$: C, 68.72; H, 7.00; N, 7.63. Found: C, 68.42; H, 6.99; N, 7.38.

[NPN]*ZrCl$_2$ (4). To a toluene solution (40 mL) of **3** (1.20 g, 1.6 mmol) was added chlorotrimethylsilane (1.77 g, 16.3 mmol). The clear yellow solution was stirred overnight and a yellow precipitate formed. The reaction was followed by ^{31}P-{^{1}H} NMR spectroscopy to ensure completion. Solvent was removed, and the resulting yellow powder was washed with pentanes (3 × 5 mL) and dried (1.04 g, 89%).

^{1}H NMR (C_6D_6, 400 MHz): δ 7.60 (dd, 2H, 7 Hz), 7.45 (d, 2H, 8 Hz), 7.05 (m, 3H), 6.91 (s, 2H), 6.84 (d, 2H, 8 Hz), 6.80 (s, 2H), and 6.05 (dd, 2H, 7 Hz) (Ar*H*), 2.46 (s, 6H), 2.34 (s, 6H), 2.09 (s, 6H), and 1.94 (s, 6H) (CH_3). ^{31}P{^{1}H} NMR (C_6D_6, 121 MHz): δ −2.8. ^{13}C{^{1}H} NMR (C_6D_6, 75 MHz): δ 159.9 ($J_{CP} = 32$ Hz), 138.5, 138.3, 137.0, 135.3, 134.6, 132.3, 132.2, 131.1, 130.8, 129.6, 125.6, 121.1, 120.6, 114.9, and 114.8 (Ar*C*), 21.1, 20.3, and 19.1 (*C*H_3). EI-MS (*m/z*): 714 (3, M^+), 541 (100, M^+ − $ZrCl_2$ − Me). Anal. Calcd for $C_{38}H_{39}N_2Cl_2PZr$: C, 63.67; H, 5.48; N, 3.91. Found: C, 63.65; H, 5.80; N, 3.98.

[NPN]*ZrCl$_2$(THF) (5). THF (1−2 drops) was added to an NMR tube with **4** (20 mg, 28 μmol) in C_6D_6 to produce a bright red-orange solution. This species was characterized by NMR spectroscopy only; coordinated THF was obscured by the excess THF present.

^{1}H NMR (C_6D_6, 300 MHz): δ 7.75 (t, 2H, 8 Hz), 7.38 (d, 2H, 8 Hz), 7.07 (m, 3H), 6.91 (s, 2H), 6.83 (s, 2H), 6.82 (d, 2H, 8 Hz), and 6.04 (dd, 2H, $J_{HH} = 7$ Hz, $J_{PH} = 6$ Hz) (Ar*H*), 2.46 (s, 6H), 2.30 (s, 6H), 2.12 (s, 6H), and 1.95 (s, 6H) (CH_3). ^{31}P{^{1}H} NMR (C_6D_6, 121 MHz): δ 2.7.

[NPN]*ZrMe$_2$ (6). To a solution of **4** (0.300 g, 0.42 mmol) in Et_2O (10 mL) at −35 °C in the dark was added methylmagnesium chloride (3.0 M in THF, 0.31 mL, 0.92 mmol) dropwise with stirring. The yellow solution was warmed to room temperature, and 1,4-dioxane (0.1 mL) was added. The solution was filtered through Celite, and the solvent was removed. Addition of pentane (5 mL) precipitated a yellow solid, which was isolated and dried under vacuum (0.225 g, 80%).

^{1}H NMR (C_6D_6, 500 MHz): δ 7.54 (m, 4H), 7.07 (m, 2H), 7.02 (m, 1H), 6.93 (s, 2H), 6.90 (d, 2H, 2 Hz), 6.88 (s, 2H), and 6.12 (t, 2H, $J_{PH} = J_{HH} = 7$ Hz) (Ar*H*), 2.51 (s, 6H), 2.14 (s, 6H), 2.09 (s, 6H), and 2.00 (s, 6H) (ArCH_3), 0.93 (d, $J_{PH} = 5$ Hz, 3H, ZrCH_3), −0.11 (s, 3H, ZrCH_3). ^{31}P{^{1}H} NMR (C_6D_6, 202.5 MHz): δ −14.1. ^{13}C{^{1}H} NMR (C_6D_6, 125.8 MHz): δ 159.4 ($J_{CP} = 33$ Hz), 139.4, 138.6, 137.5, 135.3 ($J_{CP} = 5$ Hz), 135.1 ($J_{CP} = 3$ Hz), 134.4, 132.1 ($J_{CP} = 13$ Hz), 130.9, 130.4, 129.2 ($J_{CP} = 4$ Hz), 129.1, 129.0, 128.3, 121.1 ($J_{CP} = 25$ Hz), and 114.3 ($J_{CP} = 9$ Hz) (Ar*C*), 45.1 ($J_{CP} = 6$ Hz, Zr*C*H$_3$), 41.8 ($J_{CP} = 29$ Hz, Zr*C*H$_3$), 21.1, 20.3, 19.1, and 18.9 (Ar*C*H$_3$). Anal. Calcd for $C_{40}H_{45}N_2PZr$: C, 71.07; H, 6.71; N, 4.14. Found: C, 71.35; H, 7.06; N, 4.08.

X-ray Crystal Structure Analysis. Selected crystals were coated in oil, mounted on a glass fiber, and placed under an N_2 stream. Measurements for compounds **1**·2THF and **4** were made on a Bruker X8 Apex diffractometer with graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). The data were collected at a temperature of -100 ± 1 °C. Data were collected and integrated using the Bruker SAINT[23] software package. Data were corrected for absorption effects using the multiscan technique (SADABS[24]) and for Lorentz and polarization effects. Neutral atom scattering factors were taken from Cromer and Waber.[25] Anomalous dispersion effects were included in F_{calc};[26] the values for $\Delta f'$ and $\Delta f''$ were those of Creagh and McAuley.[27] The values for the mass attenuation coefficients are those of Creagh and Hubbell.[28] All refinements were performed using the SHELXTL[29] crystallographic software package of Bruker-AXS. The structure was solved by direct methods.[30] All non-hydrogen atoms were refined anisotropically using SHELXL-97.[31] Compound **4** crystallized with two and a half molecules of benzene in the asymmetric unit. Hydrogen atoms were included in fixed positions. Structures were solved and refined using the WinGX software package version 1.64.05.[32]

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Supporting Information Available: Variable-temperature NMR spectrum of [NPN]*H_2; X-ray data for **1**·2THF and **4** are given as CIF files. This material is available free of charge via the Internet at http://pubs.acs.org.

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