# ORGANOMETALLICS

## A Novel Bis(phosphido)pyridine [PNP]<sup>2-</sup> Pincer Ligand and Its Potassium and Bis(dimethylamido)zirconium(IV) Complexes

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A novel PNP bis(secondary phosphine)pyridine pincer ligand, 2,6-bis(2-(phenylphosphino)phenyl)pyridine, has been prepared in high yield, and the properties of the doubly deprotonated form as a ligand in K<sub>4</sub>(PNP)<sub>2</sub>(THF)<sub>6</sub> and (PNP)Zr(NMe<sub>2</sub>)<sub>2</sub> have been investigated. The neutral PNP ligand has been isolated as a mixture of noninterconverting diastereomers, due to the presence of two chirogenic phosphorus atoms of the secondary phopshines, but coordination of the dianionic form to potassium and zirconium allows for isolation of a single diastereomer in near-quantitative yield. The structure of a bis(dimethylamido)zirconium(IV) derivative of the bis(phosphido)pyridine ligand and DFT calculations suggest that the phosphides do not  $\pi$ -bond to early transition metals, likely due to geometric strain and possibly orbital size mismatch between phosphorus and zirconium. As a result, the soft phosphides are prone to formation of insoluble oligomers with substantial bridging of the phosphido lone pairs to other zirconium centers.

#### Introduction

As strong, chemically inert  $\sigma$  donors, phosphines stabilize many organometallic compounds.<sup>1,2</sup> Indeed, tertiary phosphine ligands (PR<sub>3</sub>, where R = alkyl, aryl) are probably the most common neutral, L type donors. Secondary phosphines (PHR<sub>2</sub>) and their conjugate phosphides (PR<sub>2</sub><sup>-</sup>) have been much less studied as ligands, no doubt a result of their toxicity and susceptibility to autoxidation in air.<sup>3,4</sup> Using standard organic techniques to synthesize and/or purify secondary phosphines requires the extensive use of borane, oxide, sulfide, and selenide protecting groups.<sup>5–11</sup> Phosphides, generally obtained by deprotonation of a secondary phosphine or reduction of a chlorophosphine, are particularly interesting ligands, given their ability to coordinate in either an X type or LX type fashion, a

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feature common to anionic ligands with one available  $\pi$ -electron pair.<sup>12–19</sup> Unlike amide ligands, phosphides are soft donors whose lone pair resides in a more extensive orbital that can coordinate in an L type fashion to another metal in polynuclear complexes. As a consequence, many bridging phosphido complexes have been isolated, a result of long M–P bonds and reduced steric congestion, as compared with amido complexes.<sup>20–22</sup> Another feature that distinguishes phosphine (and X type phosphido) from amine (and X type amido) ligands is the high energy barrier for inversion at phosphorus, thus affording chirogenicity to asymmetrically substituted phosphines at ambient temperatures (the inversion barrier of NMe<sub>3</sub> has been estimated at 8 kcal/ mol vs 45 kcal/mol for PMe<sub>3</sub>).<sup>23</sup>

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Glueck and co-workers have reported extensively on the synthesis and structural elucidation of late-metal complexes stabilized by monodentate terminal and bridging phosphides.<sup>24–30</sup> Pincer bis(phosphides) are extremely rare, likely owing to challenges in controlling their reactivity in a many-step synthesis and isolation. In fact, to our knowledge, only one pincer bis(phosphide), a xanthene-derived P-*tert*-butylated POP pincer ligand, had been reported prior to our investigations.<sup>17</sup> We envisioned that LX<sub>2</sub> type pincer bis(phosphide)pyridines could stabilize high-valent metal complexes—particularly early-transition-metal polymerization precatalysts—via strong  $\sigma$ -donation, and potentially strong  $\pi$  donation as well.

#### **Results and Discussion**

Semirigid pyridine-linked bis(phenolate) and bis(anilide) ligands 1-4 have been previously described by our group.<sup>32-35</sup> We hoped to develop a versatile and modular synthesis of analogous bis(secondary phosphine)pyridine ligands using a sequence of cross-coupling reactions—one to establish the carbon skeleton of the ligand framework via arene—arene bond

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- (38) Alkali phenylhydrophosphide were generated in situ by depro-
- (50) Arkan phenylphosphine with 1.0 equiv of the respective hydroxide salt.



Scheme 2

construction and the other to effect a less conventional C–P coupling (Scheme 1).<sup>36–38</sup> However, slow coupling with bulky bis(triflate) **6** and eventual poisoning of the nickel and palladium catalysts by phenylphosphine encouraged us to pursue transition metal-free routes for the second step. We reasoned that the unsubstituted pyridine-linked bis(fluoride) **10**, generated by Suzuki cross-coupling of commercially available fluorophenylboronic acid **8** and dibromopyridine **9**, could provide a route to **11** through nucleophilic aromatic substitution (S<sub>N</sub>Ar) with a primary phosphide nucleophile (Scheme 2). Indeed, we were delighted to find that addition of alkalimetal phosphides to our electrophilic bis(aryl fluoride) substrate proved most successful.

The cross-coupling of 8 and 9, using  $Pd(PPh_3)_2Cl_2$  as precatalyst, cleanly affords 10 in excellent yield. As expected, no pyridine-directed activation of the C-halogen bond in 10 is observed, unlike the case for the analogous coupling reactions with (chlorophenyl)- and (bromophenyl)boronic acid analogues of 8. Treating 10 with potassium phenylhydrophosphide, generated in situ by deprotonation of PhPH<sub>2</sub> by superbasic KOH in DMSO, cleanly affords the bis-(phosphine)pyridine 11 in 70% yield. Solvent effects typical of nucleophilic substitution reactions are observed: while the reaction occurs on the order of days in nonpolar solvents, gratifyingly full conversion occurs in 20 h in DMF and 5 h in DMSO. Interestingly, the  $S_NAr$  reaction is remarkably sensitive to the counterion stabilizing the phenylhydrophosphide nucleophile. Lithium or sodium phenylhydrophosphide reacts with 10 to afford the desired bis(phosphine)





Figure 1. Selected regions of <sup>1</sup>H and <sup>31</sup>P NMR spectra in benzene- $d_6$  revealing PH(C<sub>6</sub>H<sub>6</sub>) and PH(C<sub>6</sub>H<sub>6</sub>) signals, respectively, for *rac* and *meso* diastereomers.

in only 15% or 36% yield.<sup>38</sup> A near doubling of yield was observed for the potassium salt, likely a result of softer potassium phosphide and/or subsequent side reactions that occur more readily for the lithium and sodium salts.<sup>39</sup>

Thus, bis(phosphine)pyridine 11 may be synthesized in two steps in 67% overall yield from commercially available starting material. Furthermore, the technical difficulties inherent to purifying air-sensitive secondary phosphines are avoided by the chromatography-free methods that are amenable to gram-scale synthesis. The synthesis should be modular, with opportunities to create novel PNP-pincer libraries from variously substituted (fluorophenyl)boronic acids in combination with aryl and alkyl primary phosphines.

That **11** exists as a 1:1 (benzene- $d_6$ , room temperature) mixture of *rac* and *meso* diastereomers illustrates the high energy of phosphine inversion (Figure 1).



The diagnostic <sup>1</sup>H NMR signals for the protons on the secondary phosphines of each diastereomer reveal typically large one-bond coupling to phosphorus, while the <sup>31</sup>P NMR spectrum exhibits two doublets, due to magnetically equivalent phosphorus atoms in each diastereomer, each of which couples to a

proton. The equilibrium diastereomeric ratio has not been investigated in detail, but the ratio of diasteromers does not differ greatly from one in any solvent examined thus far (CH<sub>2</sub>Cl<sub>2</sub>, THF, MeCN, PhCH<sub>3</sub>, tetrachloroethane). Variable-temperature NMR experiments reveal diastereomeric interconversion of **11** at elevated temperatures: coalescence is achieved at roughly 380 K (110 °C, <sup>1</sup>H NMR, 500 MHz, tetrachloroethane- $d_2$ ), corresponding to the rate constant  $k_{380} = 254$  s<sup>-1</sup> and free energy of activation  $\Delta G_{380}^{+} = 18.3$  kcal/mol (Figure 2).

Attempts to resolve the diastereomers were unsuccessful, and crystals of either diastereomer or cocrystallized diastereomers sufficient for X-ray structure determination could not be obtained. Fast double deprotonation of the bis-(phosphine)pyridine can be achieved quantitatively with KHMDS or benzylpotassium in THF to afford the dimeric tetrapotassium bis(bis(phosphide)pyridine) salt **12**. The presence of a single <sup>31</sup>P{<sup>1</sup>H} singlet in the NMR spectrum ( $\delta$  –14.35, 121 MHz<sup>31</sup>P{<sup>1</sup>H}, THF-*d*<sub>8</sub>) for the product immediately following deprotonation appears to indicate that both *rac* and *meso* diastereomers react with base to generate the same product in solution. Crystals of **12** were obtained from THF. X-ray analysis revealed a *C<sub>r</sub>* symmetric dimer with an octanuclear, ladderlike potassium–phosphorus core (Figure 3).

The potassium and phosphorus atoms are arranged as alternating vertices of three conjoined quadrilateral, nearly square arrays. The K atoms making up the corner vertices of the core are within bonding distances to only one P (K1-P1 = 3.2276(10) Å) but bridge weakly to the other P of the same molecule (K1-P2 = 3.5380(10) Å). Potassium atoms shared by both ligands in the center of the cluster

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Figure 2. Selected regions of <sup>1</sup>H (top) and <sup>31</sup>P{<sup>1</sup>H} (bottom) NMR spectra in tetrachloroethane- $d_2$  over a 95 K temperature range.

engage in bonding to two P atoms of one ligand (K2-P2 = 3.2479(11), K2-P1 = 3.3030(10) Å) and less strongly interact with P2 of the other ligand across the inversion center (K2-P2a = 3.3943(10) Å). The ligand pyridine ring is canted about 66° from the flanking phenyl rings to accommodate N-coordination to K1. However, the large N1-K1 internuclear distance (2.9943(19) Å) and the vector's 31° dihedral angle from the pyridine plane suggest only a weak interaction.

The propensity of phosphides to form extensive bridging networks with two or more metals appears to be the principal reason we have been unsuccessful in cleanly synthesizing high-valent early-transition-metal complexes from 11 or its dipotassium salt. For attempted preparations of group 4 metals with two simple X type (e.g., chloride or benzyl) ligands, we observed immediate precipitation of insoluble reaction products that analyzed as the desired stoichiometry, apparently due to formation of oligomers. We therefore examined homoleptic metal complexes stabilized by strong  $\pi$ -donor ancillary ligands as precursors to reduce coordinative unsaturation of the products. Indeed, we were pleased to discover that the roughly  $C_2$ -symmetric bis(phosphide)pyridine bis(dimethylamido) zirconium(IV) complex 13 can be synthesized quantitatively via treatment of  $Zr(NMe_2)_4$  with the bis(phosphine)pyridine 11 in benzene at room temperature, through a mechanism that likely involves protonolytic release of 2 equiv of dimethylamine (Scheme 3). Both enantiomers of 13 were cocrystallized for X-ray analysis from toluene. The structure reveals the desired tridentate, pincer-type interaction with the bis(phosphide)pyridine ligand (Figure 4).

(PNP)Zr(NMe<sub>2</sub>)<sub>2</sub> (13) exhibits the largest ( $C_2$  twist) torsional angle (94.13°) between the aromatic pyridine substituents observed in any of our reported  $C_2$ -symmetric



**Figure 3.** Thermal ellipsoid drawing of the solid-state structure of dimeric **12** at the 50% probability level. Hydrogens, THF carbons, and *P*-phenyl carbons have been omitted for clarity. Selected bond lengths (Å) and angles (deg): K(1)-P(2), 3.5380(10); K(1)-P(1), 3.2276(10); K(1)-N(1), 2.9943(19); K(2)-P(2), 3.2479(11); K(2)-P(1), 3.3030(10); P(2)-K(1)-P(1), 90.90(2); P(2)-K(2)-P(1), 94.91(2); K(1)-P(2)-K(2), 84.69(2); K(1)-P(1)-K(2), 88.96(2).



pyridine-linked bis(phenolate) or bis(anilide) complexes pre-pared to date (Table 1).<sup>31,34,40-42</sup> The long Zr-P bonds (2.6853(13) and 2.7002(12) Å) and nonplanarity of phosphorus, reflected by the sum of the angles around each atom  $(\sum \angle_{\mathbf{P}} = 300.28(48), 292.6(8)^\circ)$ , strongly suggest that each phosphide donates only one electron in an X-type fashion through a single bond to the metal. Phosphide  $p\pi$  to Zr  $d\pi$  donation would appear to require planarization of the ligand skeleton to allow for sp<sup>2</sup> hybridization at phosphorus, which models suggest would be highly strained with such long  $Zr-P \text{ and } P-C_{pincer} \text{ bonds} (P(1A)-C(1A) = 1.839(5), P(2A)-C(1A) = 1.839(5), P(2A) = 1.839(5), P($ C(17A) = 1.832(4) Å). Correspondingly, significant ring strain from planarization of the six-membered [-Zr-P-C-C-C-N-] rings (vide supra) is expected to make for a very high energy barrier for racemization through a C<sub>2v</sub>-symmetric intermediate. The relatively short Zr-N<sub>amide</sub> bond lengths (2.007(3) and 1.991(4) Å) and the planarity of each amide nitrogen ( $\sum \angle_N \approx 360^\circ$ ) are as expected for strong LX type bonds.

DFT calculations were performed on the frontier molecular orbitals of **13** using both 6-31G and LANL2DZ basis sets to gain further insight into the electronic structure. The HOMO reveals significant density on each phosphorus (Figure 5a). The extensive nonbonding, essentially pure 3p phosphorus orbitals suggest the ease with which (PNP)ligated metal complexes may form phosphide-bridging oligomers. In contrast, the HOMO-1 is predominantly comprised of the Zr–P  $\sigma$ -bonding interactions between the P  $\sigma$  and a well-defined Zr d<sub>z<sup>2</sup></sub> orbital; however, due to geometric strain of the ligand, the individual atomic orbitals do not achieve an ideal overlap due to the <180° Zr-P-C angles (Figure 5b). Interestingly, calculations of the LUMO reveal substantial density at the pyridine ring, suggesting that this is where reaction with a nucleophile is likely to occur (Figure 5c). While reaction with strong nucleophiles such as MeLi, NaOMe, and NaSMe may in fact occur at the pyridine ring, we obtained intractable mixtures in each case, which is unsurprising if irreversible addition of these nucleophiles eliminates aromaticity, distorts the heterocycle from planarity, and weakens the chelate to the metal.

We further explored the reactivity of complex 13 and were surprised to find that it remains stable in solution at 90 °C for 3 days, after which products of decomposition could be detected by NMR. Similarly, we observed neither reaction of the Zramide bonds with diphenylphosphine or dicyclohexylphosphine nor transamidation with diethylamine, diphenylamine, or di-p-tolylamine, even after heating at similarly elevated temperatures for 2 days. Attempts to generate an imido complex by treatment with aniline, p-fluoroaniline, and toluidine unfortunately failed as well. Perhaps most surprisingly, complex 13 does not react with 2 equiv of TMSCl at room temperature but instead reacts at 50 °C after 3 h to form a red precipitate with concomitant release of TMS(NMe<sub>2</sub>). That this precipitate is insoluble in a variety of solvents suggests that the dichloride is indeed generated but quickly oligomerizes, even under dilute conditions. These findings reveal the stability conferred upon 13 by the  $\pi$ -donating dimethylamido ligands. Disappointingly, 13 exhibited no activity as a propylene polymerization catalyst, possibly due to an excess (200-500 equiv) of the Lewis acidic cocatalyst MAO, which can coordinate to either phosphide or amide ligands.

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**Figure 4.** Thermal ellipsoid drawings of (PNP)Zr(NMe<sub>2</sub>)<sub>2</sub> (13) at the 50% probability level. Hydrogens are omitted for clarity. The left perspective is a top-down view. The right perspective is a view down the Zr–N1A bond. Selected bond lengths (Å) and angles (deg): Zr(1)–P(1A), 2.6853(13); Zr(1)–P(2A), 2.7002(12); Zr(1)–N(1A), 2.406(3); Zr(1)–N(2A), 2.007(3); Zr(1)–N(3A), 1.991(4); P(1A)–Zr(1)–P(2A), 141.26(4); Zr(1)–P(1A)–C(1A), 83.56(14); Zr(1)–P(1A)–C(18A), 115.08(15); C(18A)–P(1A)–C(1A), 102.18(19); Zr(1)–P(2A)–C(17A), 80.20(13); Zr(1)–P(2A)–C(24A), 109.76(14); C(17A)–P(2A)–C(24A), 102.7(2).

Table 1.	Comparison of Geometric	Parameters of 13 with	Those of the	Previously	Reported	Pyridine-	Linked	Bis(anilide)	and
		Bis(phenola	te) Complexe	s 14–29					



complex		М	R <sub>1</sub> , R <sub>2</sub>	$R_3, R_4, R_5$				
	Х				C1-C2-pyr	C3-C4-pyr	C1-C2-C3-C4	symmetry
<b>14</b> <sup>31</sup>	0	Ti	CMe <sub>3</sub> , CMe <sub>3</sub>	CH <sub>2</sub> Ph, -, CH <sub>2</sub> Ph	25.64	27.06	52.70	$C_2$
15 <sup>34</sup>	0	Ti	Ad, Me	OiPr, –, OiPr	36.31	32.93	63.01	$\tilde{C_2}$
<b>16</b> <sup>41</sup>	0	Та	CMe <sub>3</sub> , CMe <sub>3</sub>	NNPh <sub>2</sub> , Cl, pyridine	29.61	35.29	64.90	$\tilde{C_2}$
<b>17</b> <sup>31</sup>	0	Ti	CEt <sub>3</sub> , Me	CH <sub>2</sub> Ph, -, CH2Ph	30.69	34.31	65.00	$\tilde{C_2}$
<b>18</b> <sup>40</sup>	0	Та	CMe <sub>3</sub> , CMe <sub>3</sub>	NMe <sub>2</sub> , NMe <sub>2</sub> , NMe <sub>2</sub>	36.03	30.94	59.12	$\bar{C_2}$
<b>19</b> <sup>40</sup>	0	Та	CMe <sub>3</sub> , CMe <sub>3</sub>	NH <sub>2</sub> Ph, NHPh, NPh	38.84	27.25	69.24	$\tilde{C_2}$
<b>20</b> <sup>42</sup>	N(Mes)	Ti	H, H	$NMe_2$ , -, $NMe_2$	37.02	42.18	79.20	$\tilde{C_2}$
<b>21</b> <sup>42</sup>	N(Mes)	Zr	H, H	Cl, THF, Cl	39.01	40.24	79.25	$\tilde{C_2}$
<b>22</b> <sup>42</sup>	N(Mes)	Zr	H. H	NMe <sub>2</sub> , –, NMe <sub>2</sub>	41.53	45.78	87.31	$\tilde{C_2}$
13	PPh	Zr	H, H	$NMe_2, -, NMe_2$	43.34	50.79	94.13	$C_2$

### Conclusions

In conclusion, we have developed a short, modular, and efficient synthesis of a novel pyridine-linked precursor to a bis(phosphide) pincer ligand. The neutral ligand is an interesting system in its own right, given the presence of two chirogenic phosphorus centers. Metalation with K or Zr generates new bis(phosphide)pyridine-supported complexes. The solid-state structures reveal some very interesting sixmembered-ring strain and electronic ramifications of using semirigid, second-row,  $LX_2$  type pincer ligands in combination with more conventional first-row  $\pi$ -basic ligands such as alkylamides. To determine the possibility of inducing phosphide  $\pi$ -donation to a transition-metal center, further investigations into the coordination chemistry of this ligand and its analogues are underway.

### **Experimental Section**

General Considerations and Instrumentation. All air- and moisture-sensitive compounds were manipulated using standard high-vacuum and Schlenk techniques or manipulated in a glovebox under a nitrogen atmosphere using degassed solvents. *n*-Butyllithium solution was titrated with salicylaldehyde phenylhydrazone.<sup>43</sup> KBn was prepared according to literature methods.<sup>44</sup> Zr(NMe<sub>2</sub>)<sub>4</sub> was purchased from Strem Chemicals and sublimed prior to use. Triflic anhydride was distilled over P<sub>2</sub>O<sub>5</sub> prior to use. KOH was crushed into a fine powder using a mortar and pestle and dried overnight at 100 °C under vacuum.

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**Figure 5.** DFT-predicted MO's of  $(PNP)Zr(NMe_2)_2$  (13): (a) HOMO; (b) HOMO-1; (c) LUMO. Atoms are color-coded: turquoise, nitrogen; gray, carbon; orange, phosphorus; red, zirconium.

DMSO and DME were distilled over  $CaH_2$ . All other solvents were dried over sodium benzophenone ketyl and stored over titanocene dihyride where compatible or dried by the method of Grubbs.<sup>45</sup> All NMR solvents were purchased from Cambridge Isotopes. Benzene- $d_6$  and THF- $d_8$  were dried over sodium benzophenone ketyl, while acetonitrile- $d_3$ , methylene chloride $d_2$ , and tetrachloroethane- $d_2$  were dried over CaH<sub>2</sub> and stored over molecular sieves. Chloroform-d was used as is. All other chemicals were used as received. <sup>1</sup>H, <sup>13</sup>C, <sup>31</sup>P, and <sup>19</sup>F NMR spectra were recorded on Varian Mercury 300 or Varian IN-OVA-500 spectrometers at room temperature, unless otherwise indicated. Chemical shifts are reported with respect to internal solvent for <sup>1</sup>H and <sup>13</sup>C data: 7.16 and 128.38 (t) ppm (C<sub>6</sub>D<sub>6</sub>); 7.27 and 77.23 (t) ppm (CDCl<sub>3</sub>); 1.72 and 3.58, and 67.21 (p) and 25.37 (p) ppm (THF- $d_8$ ); 6.0 and 73.78 (t) ppm (TCE- $d_2$ ). <sup>31</sup>P chemical shifts are reported with respect to an external 85% H<sub>3</sub>PO<sub>4</sub> reference (0 ppm).

Pyridine-Linked Bis(triflate) 6. In an oven-dried 100 mL round-bottom flask equipped with a stir bar and charged with bis(phenol) 1 (2.0 g, 4.1 mmol, 1.0 equiv) was added 50 mL of Et<sub>2</sub>O. After the flask was cooled to -78 °C, *n*-butyllithium (3.6 mL, 9.0 mmol, 2.2 equiv, 2.6 M in hexane) was added dropwise. The dark red solution was warmed to room temperature and stirred for 2 h. Triflic anhydride (2.5 g, 9.0 mmol, 2.2 equiv) was added dropwise, and the reaction mixture was stirred for 16 h at room temperature. The reaction mixture was poured into ice-cold water (50 mL) and extracted three times with Et<sub>2</sub>O (50 mL). The organic extracts were washed with brine (50 mL) and dried over Na<sub>2</sub>SO<sub>4</sub>. Filtration and concentration in vacuo afforded an off-white solid. The solid was washed with petroleum ether to afford 2.8 g of analytically pure 6 (91% yield). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 1.34 (s, 18H, C(CH<sub>3</sub>)<sub>3</sub>), 1.52 (s, 18H,  $C(CH_3)_3$ ), 7.47 (d, 2H, J = 6 Hz, 3,5-NC<sub>5</sub>H- $H_2$ ), 7.54 (d, 2H, J = 3 Hz, aryl-H), 7.61 (d, 2H, J = 3 Hz, aryl-H), 7.78 (t, 1H, J = 8 Hz, 4-NC<sub>5</sub>H<sub>2</sub>-H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  31.4 (C(CH<sub>3</sub>)<sub>3</sub>), 32.0 (C(CH<sub>3</sub>)<sub>3</sub>), 35.1 (C(CH<sub>3</sub>)<sub>3</sub>), 36.4 (C(CH<sub>3</sub>)<sub>3</sub>), 118.3 (q, J = 319 Hz, ArOSO<sub>2</sub>CF<sub>3</sub>), 124.0, 127.8, 128.1, 136.1, 136.7, 141.3, 143.6, 150.9, 156.4 (aryl). <sup>19</sup>F NMR (282 MHz, CDCl<sub>3</sub>):  $\delta$  73.8 (ArOSO<sub>2</sub>CF<sub>3</sub>). HRMS (ESI): calcd mass 752.2509, exact mass 752.2526.

2,6-Bis(2'-fluorophenyl)pyridine (10). A 500 mL bomb equipped with a stir bar was charged with 2,6-dibromopyridine (6.2 g, 26 mmol, 1.0 equiv), (2-fluorophenyl)boronic acid (9.6 g, 69 m mol, 2.6 equiv), Pd(PhCN)<sub>2</sub>Cl<sub>2</sub> (0.50 g, 1.3 mmol, 0.050 equiv), and triphenylphosphine (0.68 g, 2.6 mmol, 0.10 equiv). 1,2-Dimethoxyethane was added (66 mL) to afford a canary yellow suspension, after which an aqueous solution of 4 M K<sub>2</sub>CO<sub>3</sub> (33 mL) was added. The flask was sealed and heated to 100 °C. After 16 h of stirring, the brown solution was cooled to room temperature and filtered through Celite. The brown filtrate was partitioned with EtOAc (200 mL), and the organic layer was extracted from the aqueous layer with EtOAc (100 mL) four times. The combined organic fractions were washed with brine (100 mL) and dried over MgSO<sub>4</sub>. The reaction mixture was filtered and concentrated in vacuo to afford a dark brown solid, which was redissolved in Et<sub>2</sub>O and filtered through a silica plug. The filtrate was concentrated to afford an off-white solid, which was washed with petroleum ether to afford 6.7 g of 10 in 95% yield as a white solid. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  7.18 (ddd, 2H, J = 8 Hz, J = 5 Hz, J =1 Hz), 7.26-7.32 (m, 2H), 7.35-7.44 (m, 2H), 7.77-7.87 (m, 2H), 7.79–7.81 (m, 1H), 8.15 (td, 2H,  $J_1 = 8$  Hz,  $J_2 = 2$  Hz). <sup>13</sup>C NMR  $(125 \text{ MHz}, \text{CDCl}_3): \delta 116.18 (d, J = 23 \text{ Hz}), 123.12 (d, J = 10 \text{ Hz}),$ 124.47 (d, J = 4 Hz), 127.44 (d, J = 12 Hz), 130.39 (d, J = 9 Hz),131.19 (d, J = 3 Hz), 136.787 (s), 153.05 (d, J = 2 Hz), 160.70 (d, J = 249 Hz). <sup>19</sup>F NMR (282 MHz, CDCl<sub>3</sub>):  $\delta$  117.02 (m). HRMS (FAB+) C<sub>17</sub>H<sub>12</sub>F<sub>2</sub>N: calcd mass 268.0938, measured mass 268.0942.

 $(PNP)H_2$  (11; *rac* and *meso*). In an oven-dried 250 mL roundbottom flask equipped with a stir bar and charged with powdered KOH (2.6 g, 47 mmol, 2.1 equiv) was added degassed DMSO (10 mL) and PhPH<sub>2</sub> (5.2 g, 47 mmol, 5.2 mL, 2.1 equiv). The canary yellow solution was stirred for 2 h at room temperature, followed by dropwise addition of **10** (6.0 g, 22 mmol, 1.0 equiv) as a DMSO solution (10 mL), taking care to avoid an exotherm. After 5 h of stirring, the dark red solution was quenched and diluted with an excess of degassed water (100 mL). The addition of benzene (50 mL) then afforded a slightly yellow biphasic mixture. The benzene layer was extracted into a 500 mL bomb with a cannula, and the aqueous/ DMSO layer was extracted with benzene (50 mL) two more times. The combined organic extracts were washed with

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degassed water (200 mL) four times, filtered through a pad of alumina, and concentrated in vacuo to afford a viscous oil that when taken up in Et<sub>2</sub>O and concentrated again afforded 7.0 g of 11 as a white powder in 70% yield. NMR analysis reveals a 1:1 mixture of diastereomers. <sup>1</sup>H NMR (300 MHz,  $C_6D_6$ ):<sup>41</sup>  $\delta$  5.31  $(d, J = 224 Hz, 2H, ArPH(C_6H_5)), 5.44 (d, J = 223 Hz, 6H,$ ArPH(C<sub>6</sub>H<sub>5</sub>)), 6.85-7.00 (m, 14H, aryl-, rac/meso), 7.04-7.18 (m, 14H, aryl-H, rac/meso), 7.24-7.34 (m, 6H, aryl-H, rac/ meso), 7.34-7.42 (m, 4H, aryl-H, rac/meso), 7.48-7.59 (m, 4H, aryl-H, rac/meso).  ${}^{31}P{}^{1}H{}$  NMR (121 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  -44.54 (d, J = 227 Hz), -43.85 (d, J = 224 Hz). HRMS (FAB+)C<sub>29</sub>H<sub>24</sub>NP<sub>2</sub>: calcd mass 448.1384, measured mass 448.1371.

 $(PNP)K_2$  (12a). In an oven-dried 50 mL round-bottom flask equipped with a stir bar and charged with 11 (500 mg, 1.1 mmol, 1.0 equiv) was added THF (5 mL). The clear solution was cooled to -40 °C, after which KBn (290 mg, 2.2 mmol, 2.0 equiv) dissolved in cold THF (2 mL) was added dropwise. The dark red solution was warmed to ambient temperature and concentrated in vacuo to approximately 1 mL for growth of red crystals of 12b by slow evaporation of THF into toluene. For quantitative isolation, the THF solution is completely evaporated, washed with pentane, and dried in vacuo to afford 0.58 g of the dipotassium salt as a red powder, which was stored at  $-15 \text{ °C.}^{-1}\text{H} \text{ NMR}$  (300 MHz,  $d_8$ -THF):  $\delta$  6.44 (td, J = 7.2, 1.2 Hz, 2H), 6.57–6.73 (m, 6H), 6.85 (t, J = 15.1 Hz, 4H), 7.35 (d, J = 7.6 Hz, 2H), 7.42-7.53 (m, 4H), 7.69 (t, J = 7.6 Hz, 1H), 7.72 (d, J = 7.9 Hz, 2H).<sup>31</sup>P{<sup>1</sup>H} NMR (121 MHz,  $d_8$ -THF):  $\delta - 14.35$  (s).

(PNP)Zr(NMe<sub>2</sub>)<sub>2</sub> (13). An oven-dried 50 mL round-bottom flask equipped with a stir bar was charged with bis(phosphine) 11 (57 mg, 130 µmol, 1.0 equiv) and Zr(NMe<sub>2</sub>)<sub>4</sub> (34 mg, 130 µmol, 1.0 equiv). Benzene (5 mL) was vacuum-transferred at 0 °C, and the solution was stirred rapidly while being warmed to ambient temperature. After 5 min of stirring at room temperature, the dark red solution was concentrated in vacuo to afford a red oil. Pentane was then vacuum-transferred onto the oil, and the pink suspension was concentrated in vacuo to afford 80 mg of a pink solid in quantitative yield. Crystals suitable for X-ray analysis were obtained in toluene at -35 °C. <sup>1</sup>H NMR (300 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  2.64 (s, Zr(N(CH<sub>3</sub>)<sub>2</sub>)<sub>2</sub>, 12H), 6.66 (d, J =  $7.9 \,\text{Hz}, 2\text{H}$ ,  $6.70 \,(\text{td}, J = 7.5, 1.2 \,\text{Hz}, 2\text{H})$ ,  $6.88 \,(\text{td}, J = 7.7, 1.4 \,\text{Hz})$ ,  $6.81 \,(\text{td}, J = 7.7, 1.4 \,\text{Hz})$ 2H), 6.95 (ddd, J = 7.5, 2.8, 1.3 Hz, 2H), 7.09-7.01 (m, 3H), 7.18 (t, J = 7.9 Hz, 4H), 7.47 (dd, J = 7.5, 2.8 Hz, 2H), 7.70 (t, J = 7.5 Hz, 2Hz)6.6 Hz, 4H).  ${}^{31}P{}^{1}H{}$  NMR (121 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  0.00 (br s).

Variable-Temperature NMR Procedure. All variable-temperature NMR experiments were performed on a Varian INOVA-500 spectrometer. An oven-dried J. Young NMR tube was charged with 7 mg of 11. On a high-vacuum-line setup, the tube was evacuated and 1.2 mL of tetrachloroethane- $d_2$  was vacuumtransferred onto the solid. The solution was then blanketed in argon and sealed. The desired temperature of the NMR probe was set, and after reaching said temperature, the temperature of the tube was allowed to stabilize for 15 min before acquiring a spectrum.

Table 2. Crystal and Refinement Data for Complexes 12 and 13

	12	13
empirical formula	$C_{82}H_{90}K_4N_2O_6P_4$	$C_{33}H_{33}N_3P_2Zr \cdot \frac{1}{4}C_6H_6$
formula wt	1479.84	644.31
$T(\mathbf{K})$	210(2)	100(2)
a (Å)	10.1565(12)	8.1980(9)
b(A)	11.1467(11)	33.236(4)
c(Å)	17.888(2)	23.311(2)
$\alpha$ (deg)	85.015(5)	90
$\beta$ (deg)	87.679(5)	96.280(6)
$\gamma$ (deg)	77.118(5)	90
$V(Å^3)$	1966.6(4)	6313.4(12)
Z	1	8
cryst syst	triclinic	monoclinic
space group	$P\overline{1}$	$P2_1/n$
$d_{\text{calcd}} (\text{g/cm}^3)$	1.250	1.356
$\theta$ range (deg)	2.06-26.22	1.23-25.35
$\mu (\mathrm{mm}^{-1})$	0.360	0.477
abs cor	TWINABS	semiempirical from equiv
GOF	1.627	2.255
$\mathbf{R1}^{a}, \mathbf{WR2}^{b} (I > 2\sigma(I))$	0.0560, 0.0867	0.0505, 0.0734

<sup>*a*</sup> R1 =  $\sum ||F_{o}| - |F_{c}|| / \sum |F_{o}|$ . <sup>*b*</sup> wR2 =  $[\sum [w(F_{o}^{2} - F_{c}^{2})^{2}] / \sum [w(F_{o}^{2})^{2}]^{1/2}$ .

X-ray Crystal Data: General Procedure. Crystals grown from THF (12a) and toluene (13) were removed quickly from a scintillation vial to a microscope slide coated with Paratone N oil. Samples were selected and mounted on a glass fiber with Paratone N oil. Data collection was carried out on a Bruker KAPPA APEX II diffractometer with a 0.71073 Å Mo Kα source. The structures were solved by direct methods. All nonhydrogen atoms were refined anisotropically. Some details regarding refined data and cell parameters are available in Table 2 and in the Supporting Information. Selected bond distances and angles are supplied in the captions of Figures 3 and 4.

Computational Details. Density functional calculations were carried out using Gaussian 03 Revision D.01.46 Calculations were performed using the nonlocal exchange correction by Becke<sup>47,48</sup> and nonlocal correlation corrections by Perdew,<sup>49</sup> as implemented using the b3lyp<sup>50,51</sup> keyword in Gaussian. The following basis sets were used: LANL2DZ<sup>52-54</sup> for Zr atoms and 6-31G\*\* for all other atoms. Pseudopotentials were utilized for Zr atoms using the LANL2DZ ECP. All optimized structures were verified using frequency calculations and did not contain any imaginary frequencies. Isosurface plots were made using the Visual Molecular Dynamics program.<sup>5</sup>

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mounting crystals and solving their structures. The Bruker KAPPA APEXII X-ray diffractometer was purchased via an NSF CRIF:MU award to the California Institute of Technology (Grant CHE-0639094).

**Supporting Information Available:** Figures giving NMR spectra for all compounds and tables and CIF files giving

X-ray crystallographic data data for dimeric **12** and **13**. This material is available free of charge via the Internet at http:// pubs.acs.org. Crystallographic data have also been deposited at the CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K., and copies can be obtained on request, free of charge, by quoting the publication citation and the deposition numbers 787542 and 787543.