Chelate-Enforced Phosphine Coordination Enables α-Abstraction to Give Zirconium Alkylidenes

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The rigid PNP pincer ligand (PNP = deprotonated anion of bis(*ortho*-diisopropylphoshinoaryl)amine) is shown to stabilize the $(Zr{=}CHR)^{2+}$ fragment. (PNP)Li(THF) (**2-THF**) contains P−Li bonds, as evinced by the observation of the Li−P coupling in the solution ^{31}P NMR spectrum and by the X-ray structural determination in the solid state. **2-THF** reacts with $ZrCl_4(Et_2O)_2$ to give $(PNP)ZrCl_3$ (**3**). $(PNP)ZrCl_3$ (**3**) can be alkylated with RCH_2MgCl to give $(PNP)Zr(CH_2R)_3$ (**4a**−**c**). $(PNP)ZrMe_3$ (**4a**) is thermally stable, and its solid-state structure is characterized by severe distortions from the octahedral geometry. The $(PNP)Zr(CH_2R)_3$ (R = phenyl (**4b**) or *p*-tolyl (**4c**)) compounds undergo α-abstraction at ambient temperature to give isolable Zr alkyl/alkylidenes $(PNP)Zr(=CHR)(CH_2R)$ (**5b**,**c**). The reaction follows a first-order rate law ($t_{1/2}$ at 298 K ≈ 2.3 h). The activation parameters were determined from the VT NMR studies (**4b** → **5b**): $\Delta H^{\ddagger} = 19(1)$ kcal/mol; $\Delta S^{\ddagger} = -14(3)$ cal/(mol K); $\Delta G^{\ddagger}_{298} = 23(2)$ kcal/mol. The importance of the enforcement of the phosphine coordination by the rigid PNP ligand is discussed.

In recent years, the interest in metal alkylidenes has been on the rise, largely owing to the advances in catalysis of olefin metathesis.[1−3] Alkylidene complexes of the metals of groups 5 and 6 are quite numerous.[4] Examples of alkylidenes of the group 4 metals are rare, with only a single family of stable alkylidenes known for Zr and Hf.[4−8] The most common route to alkylidenes of early transition metals involves α-hydrogen abstraction in polyalkyl compounds. This process is strongly driven by steric pressure and is therefore favored by bulkier ligands and higher coordination numbers. While for the group 5 homoleptic pentaalkyls α-abstraction to give alkylidenes is typically facile,[4] it is not so for group 4 tetraalkyls.[5f] α-Abstraction in $M(CH_2R)_4$ would generate a three-coordinate $(RCH_2)_2M{=}CHR$ (M = Ti, Zr, Hf). The available evidence indicates that three-coordinate compounds of group 4 metals with metal−element multiple bonds are exceptionally reactive (unstable).[5f,9] Ostensibly, some combination of neutral and anionic ligands is necessary to stabilize the $M{=}CR_2$ fragment (M = Ti, Zr, Hf).

Utilization of a hybrid chelating ligand is arguably the best way of introducing neutral donors into the coordination sphere of the metal in a manner that is *controlled in terms of both stereochemistry and stoichiometry*.[6−8] Since the early 1980s, the Fryzuk group has been exploring the chemistry of the signature ligands ^{Si}PNP and P_2Cp (Chart 1).[7,8,10] ^{Si}PNP and P_2Cp are conformationally flexible, and in the context of

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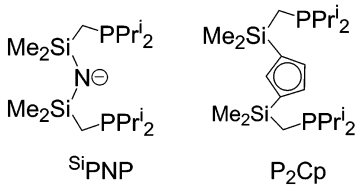
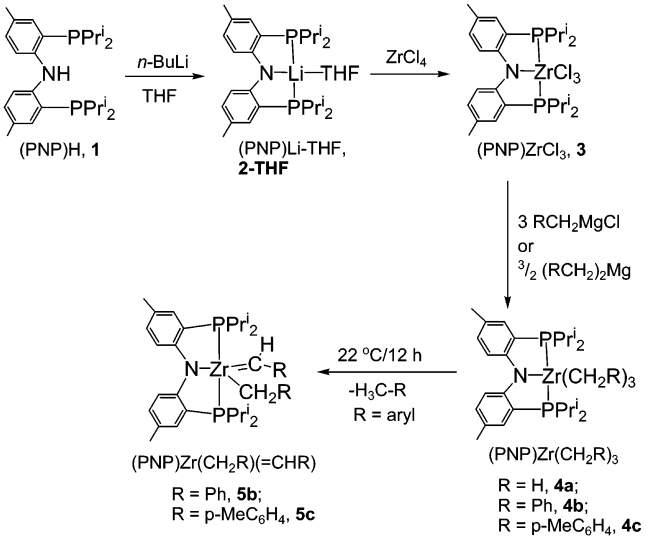
Chart 1



Scheme 1



alkylidene synthesis, this means that dissociation of the phosphine arm may be preferred to α-hydrogen abstraction as a means of alleviating steric congestion at the metal center. In $(P_2Cp)Zr(CH_2Ph)_2Cl$ only one phosphine arm is coordinated to Zr in the ground state, and thermolysis leads to α-abstraction and formation of $(P_2Cp)Zr(=CHPh)Cl$.[7] Fryzuk et al. proposed, on the basis of the kinetic evidence, that coordination of the second phosphine arms occurs in the transition state. $(P_2Cp)Zr(CH_2Ph)_3$ possesses two dangling phosphine arms and does not undergo α-abstraction to give an alkyl−alkylidene product. Hf analogues behave similarly.[8] For ^{Si}PNP, the chemistry of alkylidene formation has not been explored, but the similarity of the ^{31}P NMR chemical shift of $(^{Si}PNP)Zr(CH_2Ph)_2Cl$ to that of the free ligand indicates free phosphine arms for this compound.[11]

We have recently reported a synthesis of a new PNP ligand (Scheme 1, plain "PNP" from here on refers to the deprotonated **1**) that has a more rigid backbone than ^{Si}PNP or P_2Cp. Some of its Rh, Ir, and Pd chemistry has been communicated.[12] Two recent reports described the synthesis of the related ligand $((o\text{-}Ph_2PC_6H_4)_2N)^-$ (PNP^{Ph}).[13] The present work describes how utilization of this *rigid* pincer-type PNP ligand provides for much more favorable coordination of both phosphine arms in the ground state. This enforced Zr−P bonding leads to α-abstraction in Zr polyalkyl complexes that is much faster than in analogous complexes of P_2Cp and ultimately to unsaturated, isolable Zr alkylidenes.

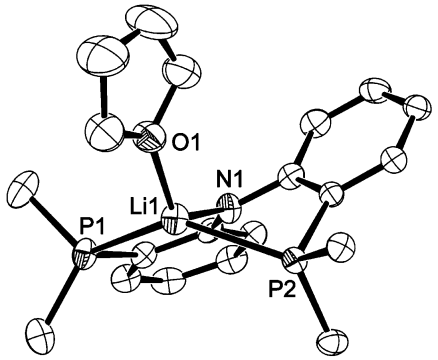


Figure 1. ORTEP drawing (30% probability ellipsoids) of **2-THF** showing selected atom labeling. Omitted for clarity: H atoms, Me groups, and disorder in the β-position of THF.

Results and Discussion

Synthesis and Structure of (PNP)Li-THF. 1 is easily deprotonated by *n*-BuLi in a variety of solvents (Scheme 1), and the Li derivative **2** can be isolated either in a donor-free form or as a mono-THF adduct (**2-THF**). The solid-state structure determination on a single crystal of **2-THF** revealed a distorted tetrahedral coordination geometry about Li (P−Li−P angle of 139.1(2)°) with a single THF donor (Figure 1).[14a,c] **2-THF** displays a well-resolved quartet in the ^{31}P NMR spectrum (δ −4.1 ppm, J_{P-Li} = 48 Hz) and a triplet in the ^{7}Li NMR spectrum (δ 2.4 ppm) in C_6D_6 at ambient temperature, while no Li−P coupling was observed for $(PNP^{Ph})Li(THF)_2$[13a] or $(^{Si}PNP)Li$.[15] This demonstrates that (a) the greater rigidity of the PNP backbone in **2-THF** versus $(^{Si}PNP)Li$ enforces Li−P interaction in **2-THF**; (b) the greater basicity and steric bulk of PPr^i_2 compared with PPh_2 leads to a stronger Li−P interaction in **2-THF** versus $(PNP^{Ph})Li(THF)_2$ and to a lower coordination number (CN) at Li. The stronger Li−P interaction in **2-THF** is also evident from the solid-state structure (Figure 1). The Li−P distances are 2.556(5) and 2.531(5) Å, ca. 0.25 Å shorter than the Li−P distances in $(PNP^{Ph})Li(THF)_2$. The Li−N (1.942(6) Å) and Li−O (1.929(6) Å) distances are also slightly (by <0.1 Å) shorter, probably as a consequence of a lower CN at Li.

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(14) (a) Crystal data for **2-THF**, $C_{30}H_{48}Li_1N_1O_1P_2$, M_r = 507.61, crystal dimensions 0.22 × 0.58 × 0.72 mm^3, monoclinic, space group *C*2/*c*, *a* = 39.230(5) Å, *b* = 9.6657(13) Å, *c* = 17.041(3) Å, β = 103.126(13)°, *V* = 6292.8(16) Å^3, *Z* = 8, ρ_{calcd} = 1.072 Mg m^{-3}, μ(Mo Kα) = 0.159 cm^{-1}, *T* = 294 K, *F*(000) = 2208, $2\theta_{max}$ = 47.4°. 4947 reflections measured, of which 4755 were unique (R_{int} = 0.01). Final R_1 = 0.0451 with wR_2 = 0.0516 for 2755 observed reflections with $I > 1.96\sigma(I)$. (b) Crystal data for **4a**, $C_{29}H_{49}N_1P_2Zr_1$, M_r = 564.88, crystal dimensions 0.22 × 0.58 × 0.58 mm^3, orthorhombic, space group *Pbcn*, *a* = 23.8250(19) Å, *b* = 14.1571(9) Å, *c* = 18.2978 (13) Å, *V* = 6171.7(8) Å^3, *Z* = 8, ρ_{calcd} = 1.216 Mg m^{-3}, μ(Mo Kα) = 0.476 cm^{-1}, *T* = 294 K, *F*(000) = 2400, $2\theta_{max}$ = 47.6°. 4702 reflections measured, of which 4693 were unique. Final R_1 = 0.0453 with wR_2 = 0.0491 for 2313 observed reflections with $I > 1.96\sigma(I)$. (c) ORTEP plots were generated using Ortep-3 for Windows. Farugia, L. J. *J. Appl. Crystallogr.* **1997**, *30*, 565.

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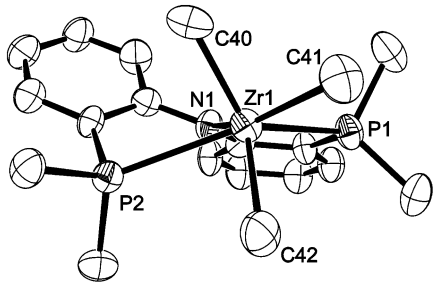

Figure 2. ORTEP drawing (50% probability ellipsoids) of **4a** showing selected atom labeling. Omitted for clarity: H atoms, Me groups except for Zr-Me. Selected distances (Å): Zr1−C40, 2.255(7); Zr1−C41, 2.285(7); Zr1−C42, 2.253(7); Zr1−P1, 2.7549(17); Zr1−P2, 2.7984(18); Zr1−N1, 2.223(4).

Synthesis and Structure of the PNP Complexes of Zr. 2-THF reacts with $ZrCl_4(OEt_2)_2$ to give (PNP)-$ZrCl_3$ (**3**) in good yield as a sparingly soluble red solid. The ^{31}P NMR chemical shift of **3** (27.1 ppm), which lies considerably downfield from **1** or **2**, is indicative of the coordination of the phosphine arms to Zr. The overall symmetry displayed by **3** in its ^{31}P, ^{1}H, and ^{13}C NMR spectra is C_2 or C_s. An idealized facial-PNP coordination can be ruled out on the basis of the observation of doublets of virtual triplets for the Me groups of the PPr^i_2 moieties.[16] In addition, the frame of this PNP ligand is clearly more adapted to a meridional configuration. Even for the more flexible Fryzuk's ligands, the meridional coordination was found for the bulkier (^{Si}PNP)MCl_3 (M = Zr, Hf) in the solid state.[17] The solid-state structure of (PNP)PdCl is C_2-symmetric owing to the twist in the backbone of the chelate.[12a] While (PNP)PdCl is C_{2v}-symmetric in solution, implying facile interconversion between degenerate C_2 conformers, such interconversion in (PNP)$ZrCl_3$ (**3**) may be slowed by the extra chlorides attached to the metal. An alternative explanation is that **3** has a structure similar to that of (PNP)$ZrMe_3$ (**4a**, vide infra) but with stronger P−Zr bonds (and hence larger $^2J_{P-P}$ coupling) because of the higher Lewis acidity of Zr in **3**.

Alkylation of **3** with 3−3.5 equiv of RCH_2MgCl (R = H, Ph, *p*-MeC_6H_4) or a corresponding amount of $(RCH_2)_2Mg$ leads to the formation of (PNP)$Zr(CH_2R)_3$ (**4a**−**c**) in >85% yield (in situ by ^{31}P NMR). An X-ray structure determination revealed a highly distorted geometry about Zr in **4a** (Figure 2).[14b,c] The overall geometry is reminiscent of the structure of (^{Si}PNP)-$HfMe_3$.[18] For the latter, the description of a twice phosphine-capped N-$HfMe_3$ tetrahedron was deemed appropriate. In the case of the N-$ZrMe_3$ substructure in **4a**, this description fails: the angles deviate from tetrahedral values to a much greater extent (82°−142°) and the P−Zr−P angle (134.33(5)°) is larger than the P−Hf−P angle (ca. 115°) in (^{Si}PNP)$HfMe_3$ (here ^{Si}PNP has PMe_2 arms, see Chart 1). Both the PNP and the Me_3 sets of donors in **4a** are halfway between a facial and a meridional arrangement. It is not clear whether the structural differences between (^{Si}PNP)$HfMe_3$ and **4a** stem from the difference in the rigidity of the PNP ligand, the difference in the bulk of the phosphine substituents, or both. A regular, *mer*-(PNP)$ZrMe_3$ structure seems sterically sound, but is probably avoided to maximize Zr−Me σ-bonding and, in particular, to escape placement of two Me groups *trans* to each other. Polyalkyl compounds with d^0 metal centers often display related electronic structural distortions.[19]

It is telling that the phosphine arms were found to coordinate strongly to Li (**2-THF**) and Zr (**4a**) in the solid state. Both Li^I and Zr^{IV} are hard acids and generally would have little affinity for the bulky, soft phosphine donors. We view the observed phosphine coordination as evidence that the relative rigidity of the PNP ligand enforces phosphine coordination. The rotation about the N−C bond may move the phosphine away from the metal in a PNP complex, but even a dihedral angle between the aromatic rings of ca. 59° (**4a**) is compatible with metal−phosphorus bonding.

Solution NMR studies indicate average C_2 or C_s symmetry for the PNP ligand in **4a**−**c** and show that all three Zr-CH_2R groups are equivalent. In contrast to **3**, the ^{1}H resonances of the methyls of the ^{i}Pr groups are doublets of doublets and not doublets of virtual triplets. The observed equivalence of the alkyl groups cannot be reconciled with the static structure found in the solid state or any other *static* structure. Fryzuk et al. outlined several possible fluxional processes for (^{Si}PNP)MMe_3 (M = Zr, Hf); the same are possible for **4**.[18] Consistent with a non-*trans* disposition of phosphine arms, virtual triplet fine structures are *not* observed for the ^{1}H and ^{13}C NMR signals of **4a**−**c** in solution.[16] The chemical shifts of the ^{31}P resonances of **4a**−**c** are similar to each other (δ ca. 13 ppm) and different from those of **1** or **2**, indicating that the phosphines in **4b**,**c** are bound to Zr. Presumably, **4a**−**c** are structurally similar.

While **4a** is thermally stable (no NMR-detectable change after 5 h at 80 °C in C_6D_6), **4b**,**c** slowly evolve in solution at ambient temperature into the alkyl−alkylidene compounds **5b**,**c** with concomitant production of toluene or *p*-xylene. Compounds **5b**,**c** are stable at ambient temperature in solution and in the solid state. The definitive spectroscopic feature of **5** is the presence of a downfield alkylidene signal in the ^{13}C NMR spectrum (δ 231.0 (**5b**), 230.6 (**5c**)).[4] The low value (92 Hz) of the alkylidene $^1J_{CH}$ coupling constant in an undecoupled ^{13}C NMR spectrum is indicative of an α-agostic alkylidene.[4] The signals for the Zr-CH_2-R carbons in the undecoupled ^{13}C NMR spectra experiments are each a triplet (δ 60.3, J_{CH} = 131 Hz for **5b**; δ 59.0, J_{CH} = 132 Hz for **5c**). The alkylidene H resonates at δ 7.32 (7.11) in **5b** (**5c**). These data for **5** are similar to those reported for (P_2Cp)Zr=CHPh(Cl).[7] An AB pattern is observed for **5b**,**c** in the ^{31}P NMR spectrum. The J_{PP} value of ca. 60 Hz in **5b**,**c** is smaller than the typical *trans*-J_{PP} values (100−300 Hz) and is indicative of a P−M−P angle substantially smaller than 180°.[16]

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Unfortunately, our multiple attempts at growing X-ray quality single crystals of **5b** or **5c** have been unsuccessful. However, the spectroscopic data in solution clearly establish the proposed alkylidene formulation with a dissymmetric, five-coordinate environment about Zr, and the empirical formula is supported by elemental analysis. In a reaction expected for an early metal alkyl/alkylidene, **5b**,**c** react with $(CX_3)_2CO$ to give as organic products $(CX_3)_2C{=}CH{-}R$ and RCH_2X (X = H, D) (see Supporting Information). The fate of Zr has not been determined, although excess acetone liberates ligand **1**.

Kinetic Studies. We used VT NMR to interrogate the kinetics of the transformation of **4b** into **5b**. The reaction was found to follow the first-order rate law $d(\ln[\mathbf{4b}]) = -k \times dt$ over the studied 20−53 °C range ($k_{298} = 8.4(4) \times 10^{-5}$ s^{-1}; $t_{1/2}(298\ \text{K}) \approx 2.3$ h). Activation parameters were determined from the Eyring plot: $\Delta H^{\ddagger} = 19(1)$ kcal/mol; $\Delta S^{\ddagger} = -14(3)$ cal/(mol K); $\Delta G^{\ddagger}_{298} = 23(2)$ kcal/mol. The comparison with the kinetic data for the α-abstraction in $(P_2Cp)Zr(CH_2Ph)_2Cl$ is insightful.[7b] The conversion of **4b** to **5b** is much faster; the 298 K rate for **4b** corresponds to the rate at 343 K for $(P_2Cp)Zr(CH_2Ph)_2Cl$. The $\Delta S^{\ddagger}$ for the reaction of **4b** is *less negative* than the −22 eu value for the Fryzuk's $(P_2Cp)Zr(CH_2Ph)_2Cl$. $(P_2Cp)Zr(CH_2Ph)_2Cl$ has *only one* Zr−P bond in the ground state. Fryzuk et al. concluded that in the α-abstraction in $(P_2Cp)Zr(CH_2Ph)_2Cl$ part of the entropic contribution to the activation barrier corresponds to the need to coordinate *both* phosphine arms in the transition state.[7b] Notably, $(P_2Cp)Zr(CH_2Ph)_3$ has *neither* of the phosphine arms coordinated to Zr in the ground state, and it is thermally stable.[7] From this perspective, our results, particularly the less negative $\Delta S^{\ddagger}$, are consistent with the enforcement of phosphine coordination by the rigid PNP ligand *in the ground state* and throughout the reaction coordinate. The activation barrier for α-abstraction is thus lowered ostensibly by decreasing the unfavorable $\Delta S^{\ddagger}$ contribution.

Conclusion

It is well known that chelating ligands often encourage reactivity at the metal centers that is different from analogous complexes with monodentate ligands. However, the rigidity of otherwise similar chelating ligands may lead to drastic differences in reactivity as well.[20] In the present report the favored coordination of the phosphine arms of the PNP chelate leads to the facilitation of α-abstraction and isolation of rare zirconium alkylidenes under ambient conditions. Kinetic studies indicate the importance of entropic considerations. Future studies will be aimed at the exploration of the generality of this approach to group 4 alkylidenes and their reactivity.

Experimental Section

General Considerations. Unless specified otherwise, all manipulations were performed under an argon atmosphere using standard Schlenk or glovebox techniques. Pentane, toluene, diethyl ether, tetrahydrofuran, and C_6D_6 were dried over sodium-benzophenone ketyl, distilled or vacuum transferred, and stored over molecular sieves. Dichloromethane was dried over calcium hydride prior to a final distillation under an Ar atmosphere. CD_2Cl_2 was dried over calcium hydride, then vacuum transferred and stored over molecular sieves prior to use. Acetone-d_6 was dried over molecular sieves and then vacuum transferred. (PNP)H (**1**),[12a] $Mg(CH_2Ph)_2{\cdot}2THF$,[21] and $MgMe_2$[22] were prepared according to published procedures. $ZrCl_4{\cdot}2Et_2O$ was prepared by adding 4 equiv of ether to a CH_2Cl_2 slurry of $ZrCl_4$, filtering, and pumping the filtrate to dryness to give the product as a white powder. All other chemicals were used as received from commercial vendors. NMR spectra were recorded on a Varian iNova 400 spectrometer (^{1}H NMR, 399.755 MHz; ^{13}C NMR, 100.518 MHz; ^{31}P NMR, 161.822 MHz) or a Varian iNova 500 spectrometer (^{7}Li NMR, 194.205 MHz). Chemical shifts are reported in δ (ppm). For ^{1}H and ^{13}C NMR spectra, the residual solvent peak was used as an internal reference. ^{31}P NMR spectra were referenced externally using 85% H_3PO_4 at δ 0 ppm. ^{7}Li NMR spectra were referenced to the peak of 1 M LiCl in D_2O at δ 0 ppm.

(PNP)Li (2). (PNP)H (**1**) (119 mg, 0.275 mmol) was suspended in 20 mL of pentane and cooled to −35 °C. *n*-BuLi (111 μL, 0.275 mmol, 2.5 M in hexane) was slowly added via syringe. The reaction mixture was allowed to warm to ambient temperature and stirred for 2 h. The volatiles were removed under reduced pressure, and the residue was dissolved in cold pentane. The clear, yellow solution was placed into a −35 °C freezer, and after 12 h, the yellow microcrystalline solid formed was collected by filtration and then dried in vacuo. Yield: 77 mg, 64%. ^{1}H NMR (C_6D_6): δ 7.45 (br, 2H, Ar-*H*), 6.99 (s, 2H, Ar-*H*), 6.94 (d, 2H, $^3J_{HH} = 8$ Hz, Ar-*H*), 2.26 (s, 6H, Ar-*Me*), 1.93 (m, 4H, C*H*Me$_2$), 1.06 (dd, 12H, $^3J_{PH} = 14$ Hz, $^3J_{HH} = 7$ Hz, CH*Me*$_2$), 0.94 (dd, 12H, $^3J_{PH} = 12$ Hz, $^3J_{HH} = 7$ Hz, CH*Me*$_2$). ^{13}C{^{1}H} NMR (C_6D_6): δ 163.9 (m), 133.0 (s), 131.9 (s), 123.0 (s), 120.3 (m), 119.7 (m), 22.6 (s, *C*HMe$_2$), 20.9 (s, Ar-*C*H$_3$), 20.1 (d, $^2J_{PC} = 12$ Hz, CH*Me*$_2$), 19.7 (d, $^2J_{PC} = 8$ Hz, CH*Me*$_2$). ^{31}P{^{1}H} NMR (C_6D_6): δ −4.4 (s). ^{7}Li NMR (C_6D_6): δ 3.2 (br). Anal. Calcd (Found) for $C_{26}H_{40}NP_2Li$: C, 71.71 (71.62); H, 9.26 (9.30).

(PNP)Li·THF (2-THF). *n*-Butyllithium (3.13 mL, 7.80 mmol, 2.5 M in hexane) was slowly added to a cooled (−35 °C) solution of **1** (2.11 g, 4.87 mmol) in 30 mL of THF. The mixture was stirred at ambient temperature for 2 h, and then all volatiles were removed in vacuo. The residue was triturated with 20 mL of pentane and then placed into a −35 °C freezer. After 8 h, the resulting yellow solid was filtered off and dried under vacuum. Total yield: 2.07 g (83%). ^{1}H NMR (C_6D_6): δ 7.62 (dd, 2H, $^3J_{HH} = 8$ Hz, $^3J_{PH} = 6$ Hz, Ar-*H*), 7.05 (s, 2H, Ar-*H*), 6.99 (d, 2H, $^3J_{HH} = 8$ Hz, Ar-*H*), 3.37 (t, 4H, $^3J_{HH} = 6$ Hz, OC*H*$_2$CH$_2$), 2.31 (s, 6H, Ar-*Me*), 2.00 (m, 4H, C*H*Me$_2$), 1.16 (t, 4H, $^3J_{HH} = 6$ Hz, OCH$_2$C*H*$_2$), 1.12 (dd, 12H, $^3J_{PH} = 15$ Hz, $^3J_{HH} = 8$ Hz, CH*Me*$_2$), 1.06 (dd, 12H, $^3J_{PH} = 13$ Hz, $^3J_{HH} = 7$ Hz, CH*Me*$_2$). ^{13}C{^{1}H} NMR (C_6D_6): δ 161.2 (d, $J_{PC} = 19$ Hz), 132.8 (d, $J_{PC} = 2$ Hz), 131.6 (s), 121.4 (d, $J_{PC} = 2$ Hz), 119.4 (d, $J_{PC} = 10$ Hz), 116.5 (d, $J_{PC} = 4$ Hz), 68.3 (s, O*C*H$_2$CH$_2$), 25.2 (s, OCH$_2$*C*H$_2$), 22.7 (d, *C*HMe$_2$, $J_{CP} = 2$ Hz), 21.1 (s, Ar-*C*H$_3$), 20.2 (d, $J_{CP} = 14$ Hz, CH*Me*$_2$), 19.7 (d, $J_{CP} = 9$ Hz, CH*Me*$_2$). ^{31}P{^{1}H} NMR (C_6D_6): δ −4.1 (q, $^1J_{LiP} = 48$ Hz). ^{7}Li NMR (C_6D_6): δ 2.4 (t, $^1J_{LiP} = 48$ Hz).

(PNP)ZrCl$_3$ (3). To $ZrCl_4{\cdot}2Et_2O$ (0.991 g, 2.60 mmol) suspended in cold toluene (30 mL, −35 °C) was added a cold toluene solution (20 mL, −35 °C) of **2-THF** (1.33 g, 2.60 mmol). The resulting mixture was stirred at ambient temperature for 12 h. All volatiles were then removed in vacuo. The residue was extracted with 65 mL of CH_2Cl_2 and then passed through

(20) For an example of the influence of the rigidity of the bidentate phosphine on the reactivity of (P−P)PtMe$_4$ complexes (P−P = $Ph_2PCH_2CH_2PPh_2$ or *o*-$C_6H_4(PPh_2)_2$) see: Crumpton-Bregel, D. M.; Goldberg, K. I. *J. Am. Chem. Soc.* **1997**, *119*, 10696.

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a glass frit lined with Celite to remove LiCl. The solvent was removed in vacuo from the filtrate to yield a red solid (1.38 g, 85% yield). ^{1}H NMR (CD_2Cl_2): δ 7.09 (s, 2H, Ar-*H*), 7.03 (d, 2H, $^3J_{HH}$ = 8 Hz, Ar-*H*), 6.65 (d, 2H, $^3J_{HH}$ = 8 Hz), 2.77 (br, 2H, C*H*Me$_2$), 2.39 (br, 2H, C*H*Me$_2$), 2.29 (s, 6H, Ar-*Me*), 1.49 (app. q, dvt, J_{PH} = 8 Hz, $^3J_{HH}$ = 7 Hz, CH*Me$_2$*), 1.40 (app. q, dvt, J_{PH} = 8 Hz, $^3J_{HH}$ = 7 Hz, CH*Me$_2$*), 1.22 (m, 12H, CH*Me$_2$*). ^{13}C NMR (CD_2Cl_2): δ 159.8 (br), 133.3 (s), 132.1 (s), 122.1 (br), 120.1 (s), 26.9 (br, *C*HMe$_2$), 22.2 (br, *C*HMe$_2$), 21.0 (s, Ar-*Me*), 20.4 (s, CH*Me$_2$*), 18.9 (s, two peaks overlapped, CH*Me$_2$*), 17.8 (s, CH*Me$_2$*). ^{31}P{^{1}H} NMR (CD_2Cl_2): δ 27.1 (s). Anal. Calcd (Found) for $C_{26}H_{40}NP_2Cl_3Zr$: C, 50.08 (49.47); H, 6.42 (6.65); Cl, 16.85 (16.19).

(PNP)ZrMe$_3$ (4a). Compound **3** (420 mg, 0.670 mmol) was suspended in 30 mL of ether and cooled to −35 °C. To this suspension were added 114 μL of dioxane and $MgMe_2$ (72 mg, 1.30 mmol) to result in gradual dissolution of **3**. The color of the solution slowly changed to bright yellow. The mixture was stirred at room temperature for 4 h. After that, volatiles were removed in vacuo. The residue was extracted with pentane and passed through a pad of Celite. The filtrate was stored in a freezer (−35 °C) for 2 h. The supernatant was decanted, and the pale yellow crystalline solid was dried under vacuum to afford 120 mg of product (31% yield). ^{1}H NMR (C_6D_6): δ 7.00 (dd, 2H, $^3J_{HH}$ = 8 Hz, $^4J_{PH}$ = 4 Hz, Ar-*H*), 6.92 (d, 2H, $^3J_{PH}$ = 4 Hz, Ar-*H*), 6.85 (d, 2H, $^3J_{HH}$ = 8 Hz, Ar-*H*), 2.29 (m, 2H, C*H*Me$_2$), 2.23 (m, 2H, C*H*Me$_2$), 2.11 (s, 6H, Ar-*Me*), 1.23 (dd, 6H, $^3J_{PH}$ = 14 Hz, $^3J_{HH}$ = 7 Hz, CH*Me$_2$*), 1.14 (dd, 6H, $^3J_{PH}$ = 16 Hz, $^3J_{HH}$ = 7 Hz, CH*Me$_2$*), 1.10 (dd, 6H, $^3J_{PH}$ = 16 Hz, $^3J_{HH}$ = 7 Hz, CH*Me$_2$*), 1.00 (t, J_{PH} = 4 Hz, 9H, Zr*Me$_3$*), 0.94 (dd, 6H, $^3J_{PH}$ = 10 Hz, $^3J_{HH}$ = 7 Hz, CH*Me$_2$*). ^{13}C{^{1}H} NMR (C_6D_6): δ 160.7 (m), 132.9 (s), 132.3 (s), 127.9 (s), 121.0 (m), 120.7 (m), 51.7 (t, J_{PC} = 2 Hz, Zr*Me$_3$*), 24.5 (br, *C*HMe$_2$), 21.7 (dd, J = 4 Hz, J = 6 Hz, *C*HMe$_2$), 21.1 (s, Ar*C*H$_3$), 20.1 (m, CH*Me$_2$*), 19.9 (m, CH*Me$_2$*), 18.8 (m, CH*Me$_2$*), 17.3 (s, CH*Me$_2$*). ^{31}P{^{1}H} NMR (C_6D_6): δ 13.0 (s). ^{1}H{^{31}P} NMR (C_6D_6): δ 7.01 (d, 2H, $^3J_{HH}$ = 8 Hz, Ar-*H*), 6.92 (br, 2H, Ar-*H*), 6.85 (dd, 2H, $^3J_{HH}$ = 8 Hz, $^4J_{HH}$ = 2 Hz, Ar-*H*), 2.28 (m, 2H, C*H*Me$_2$), 2.21 (m, 2H, C*H*Me$_2$), 2.11 (s, 6H, Ar−C*H$_3$*), 1.23 (d, 6H, $^3J_{HH}$ = 7 Hz, CH*Me$_2$*), 1.14 (d, 6H, $^3J_{HH}$ = 7 Hz, CH*Me$_2$*), 1.10 (d, 6H, $^3J_{HH}$ = 7 Hz, CH*Me$_2$*), 0.98 (s, 9H, Zr*Me$_3$*), 0.95 (d, 6H, $^3J_{HH}$ = 7 Hz, CH*Me$_2$*). Anal. Calcd (Found) for $C_{29}H_{49}NP_2Zr$: C, 61.81 (61.60); H, 8.70 (8.87).

(PNP)Zr(CH$_2$Ph)$_3$ (4b). To a cooled (−35 °C) ether slurry of **3** (27.3 mg, 0.043 mmol) was added 22.6 μL of dioxane, followed by $Mg(CH_2Ph)_2$·2THF (21.9 mg, 0.064 mmol). The red color of the slurry became orange in 2 min. The volatiles were then removed in vacuo. The NMR sample was prepared by dissolving the residue in C_6D_6 and then filtering. The ^{31}P NMR analysis showed that **4b**, (PNP)MgCl, and **5b** were present in a 85:10:5 ratio. ^{1}H NMR (C_6D_6): δ 7.12 (d, 4H, $^3J_{HH}$ = 8 Hz, Ar-*H*), 7.01−6.90 (m, 17H, Ar-*H*), 2.82 (d, 3H, $^3J_{HH}$ = 10 Hz, ZrC*H$_2$*Ph), 2.71 (d, 3H, $^3J_{HH}$ = 10 Hz, ZrC*H$_2$*Ph), 2.12 (s, 6H, Ar-*Me*), 2.13−2.00 (m, 2H, C*H*Me$_2$), 1.04 (dd, 6H, J_{PH}= 15 Hz, $^3J_{HH}$ = 7 Hz, CH*Me$_2$*), 0.96 (m, 12H, CH*Me$_2$*), 0.87 (m, 6H, CH*Me$_2$*). ^{13}C{^{1}H} NMR (C_6D_6): δ 149 (s), 132.5 (d, J = 1 Hz), 129.0 (s), 128.7 (s), 128.5 (s), 127.8 (s), 121.6 (s), 78.0 (s, Zr*C*H$_2$Ph), 25.6 (s, *C*HMe$_2$), 25.1 (s, *C*HMe$_2$), 22.3 (s, CH*Me$_2$*), 20.8 (s, Ar-*Me*), 18.9 (s, CH*Me$_2$*), 18.8 (s, CH*Me$_2$*), 18.4 (s, CH*Me$_2$*). ^{31}P{^{1}H} NMR (C_6D_6): δ 12.9 (s).

After 12 h, compound **4b** was fully transferred into **5b**. The resulting mixture contains (by ^{31}P NMR) compound **5b** (85%), (PNP)MgCl (10%), and traces of unidentified compounds.

Observation of 4c by NMR. To a cooled (−35 °C) ether slurry of **3** (53.6 mg, 0.084 mmol) was added 20 μL of dioxane, followed by 4-methylbenzylmagnesium chloride (0.52 mL, 0.26 mmol, 0.5 M in THF). The red color of the slurry became orange in 2 min. The volatiles were then removed in vacuo. The NMR sample was prepared by dissolving the residue in cold pentane (−35 °C), then pumping pentane solution to dryness and redissolving in C_6D_6. The ^{31}P NMR analysis showed that **4c** constituted ca. 80% of the resulting mixture. ^{1}H NMR (C_6D_6): 2.80 (d, 3H, $^3J_{HH}$ = 10 Hz, ZrC*H$_2$*Ph), 2.66 (d, 3H, $^3J_{HH}$ = 10 Hz, ZrC*H$_2$*Ph). ^{31}P{^{1}H} NMR (C_6D_6): δ 12.2 (s). ^{13}C{^{1}H} NMR (C_6D_6): δ 77.2 (s). Identification and assignment of the full set of the ^{1}H and ^{13}C NMR resonances of **4c** was not possible because of the presence of the (PNP)MgCl and other, unidentified minor impurities.

(PNP)Zr(=CHPh)(CH$_2$Ph) (5b). $Mg(CH_2Ph)_2$·2THF (187 mg, 0.556 mmol) was added to **3** (219 mg, 0.348 mmol) suspended in toluene (30 mL) with 180 μL of dioxane. The mixture was stirred for 16 h, and then all volatiles were removed under vacuum. The residue was extracted with pentane and filtered. The pentane solution was pumped to dryness to afford the crude **5b** (90% pure by NMR). The analytically pure **5b** can be obtained by recrystallization from cold pentane. Yield: 131 mg (53%). ^{1}H NMR (C_6D_6): δ 7.32 (s, 1H, ZrC*H*Ph), 7.10−6.89 (m, 10H, Ar-*H*), 6.85 (br s, 2H, Ar-*H*), 6.76−6.70 (m, 3H, Ar-H), 6.60 (t, 1H, J = 7 Hz), 3.06 (d, 1H, $^2J_{HH}$ = 9 Hz, ZrC*H$_2$*Ph), 2.60 (dd, 1H, $^2J_{HH}$ = 9 Hz, J = 4 Hz, ZrC*H$_2$*Ph), 2.33 (m, 1H, C*H*Me$_2$), 2.15 (s, 3H, Ar-*Me*), 2.13 (s, 3H, Ar-*Me*), 2.20−2.00 (m, 2H, C*H*Me$_2$), 1.43 (m, 1H, C*H*Me$_2$), 1.25 (dd, 3H, J = 7 Hz, J = 15 Hz, CH*Me$_2$*), 1.19 (dd, 3H, J = 7 Hz, J = 15 Hz, CH*Me$_2$*), 1.14 (dd, 3H, J = 7 Hz, J = 14 Hz, CH*Me$_2$*), 1.08 (dd, 3H, J = 7 Hz, J = 16 Hz, CH*Me$_2$*), 0.94 (dd, 3H, J = 7 Hz, J = 15 Hz, CH*Me$_2$*), 0.86 (dd, 3H, J = 7 Hz, J = 15 Hz, CH*Me$_2$*), 0.77 (dd, 3H, J = 7 Hz, J = 9 Hz, CH*Me$_2$*), 0.67 (dd, 3H, J = 7 Hz, J = 16 Hz, CH*Me$_2$*). ^{13}C{^{1}H} NMR (C_6D_6): δ 230.7 (s, Zr*C*HPh), 160.0 (dd, J = 2 Hz, J = 24 Hz), 158.2 (dd, J = 2 Hz, J = 20 Hz), 148.9 (s), 139.3 (s), 133.1 (d, J = 1 Hz), 132.6 (s), 132.5 (dd, J = 2 Hz, J = 8 Hz), 130.2 (s), 129.3 (s), 128.7 (d, J = 4 Hz), 128.5 (s), 128.4 (d, J = 4 Hz), 127.7(s), 126.0 (s), 123.2 (d, J = 22 Hz), 122.2 (s), 120.5 (d, J = 7 Hz) 120.0 (s), 119.3 (d, J = 7 Hz), 116.1 (d, J = 21 Hz), 60.3 (s, Zr*C*H$_2$Ph), 27.0 (d, J = 10 Hz, *C*HMe$_2$), 22.9 (d, J = 6 Hz, *C*HMe$_2$), 21.2 (d, J = 18 Hz, *C*HMe$_2$), 20.9 (d, J = 6 Hz, *C*HMe$_2$), 20.8(s, Ar-*C*H$_3$), 20.7 (s, Ar-*C*H$_3$), 20.6 (d, J = 7 Hz, CH*Me$_2$*), 19.6 (d, J = 7 Hz, CH*Me$_2$*), 19.5 (d, J = 10 Hz, CH*Me$_2$*), 19.4 (d, J = 4 Hz, CH*Me$_2$*), 19.1 (d, J = 10 Hz, CH*Me$_2$*), 18.5 (d, J = 11 Hz, CH*Me$_2$*), 17.5 (s, CH*Me$_2$*), 15.2 (d, J = 7 Hz, CH*Me$_2$*). ^{31}P{^{1}H} NMR (C_6D_6): δ 28.6 (d, J = 59 Hz), 26.6 (d, J = 59 Hz). The selected undecoupled ^{13}C NMR data follow: δ 230.7 (d, $^1J_{CH}$ = 92 Hz, Zr*C*HPh), 60.3 (t, $^1J_{CH}$ = 131 Hz, Zr*C*H$_2$Ph). The selected ^{1}H NMR data collected while decoupling the ^{31}P signal at 28.5 ppm follow: 2.62 (d, 1H, J = 9 Hz, ZrC*H$_2$*Ph), 1.25 (d, 3H, J = 7 Hz, CH*Me$_2$*), 1.19 (d, 3H, J = 7 Hz, CH*Me$_2$*), 1.14 (d, 3H, J = 7 Hz, CH*Me$_2$*), 1.08 (d, 3H, J = 6 Hz, CH*Me$_2$*), 0.94 (d, 3H, J = 7 Hz, CH*Me$_2$*), 0.86 (d, 3H, J = 7 Hz, CH*Me$_2$*), 0.77 (d, 3H, J = 7 Hz, CH*Me$_2$*), 0.67 (d, 3H, J = 7 Hz, CH*Me$_2$*). Anal. Calcd (Found) for $C_{40}H_{53}NP_2Zr$: C, 68.53 (68.49); H, 7.62 (7.76).

(PNP)Zr(=CHC$_6$H$_4$Me)(CH$_2$C$_6$H$_4$Me) (5c). A solution of 4-methylbenzylmagnesium chloride in THF (0.5 M, 4.77 mL, 2.40 mmol) was added dropwise to **3** (498 mg, 0.800 mmol) suspended in 40 mL of ether with 0.42 mL of dioxane. The workup procedure was similar to that for **5b**. Yield: 286 mg (50%). ^{1}H NMR (C_6D_6): δ 7.11 (s, 1H, ZrC*H*C$_6$H$_4$Me), 7.10 (dd, 1H, J = 7 Hz, J = 4 Hz, Ar-*H*), 7.02 (dd, 1H, J = 8 Hz, J = 4 Hz, Ar-*H*), 6.98−6.91 (m, 2H, Ar-*H*), 6.90−6.80 (m, 8H, Ar-*H*), 6.68 (d, 2H, J = 8 Hz, Ar-*H*), 3.07(d, 1H, $^1J_{HH}$ = 9 Hz, ZrC*H$_2$*C$_6$H$_4$Me), 2.60 (dd, 1H, J = 4 Hz, $^1J_{HH}$ = 9 Hz, ZrC*H$_2$*C$_6$H$_4$Me), 2.32 (m, 1H, C*H*Me$_2$), 2.17 (s, 3H, Ar-*Me*), 2.15 (s, 3H, Ar-*Me*), 2.14(s, 3H, Ar-*Me*), 2.15−2.10 (m, 2H, C*H*Me$_2$), 2.07(s, 3H, Ar-*Me*), 1.44(m, 1H, C*H*Me$_2$), 1.28 (dd, 3H, J = 7 Hz, J = 15 Hz, CH*Me$_2$*), 1.21 (dd, 3H, J = 6 Hz, J = 12 Hz, CH*Me$_2$*) 1.16 (dd, 3H, J = 7 Hz, J = 11 Hz, CH*Me$_2$*), 1.13 (dd, 3H, J = 7 Hz, J = 14 Hz, CH*Me$_2$*), 0.97 (dd, 3H, J = 7 Hz, J = 11 Hz, CH*Me$_2$*), 0.89 (dd, 3H, J = 7 Hz, J = 16 Hz, CH*Me$_2$*), 0.80 (dd, 3H, J = 7 Hz, J = 8 Hz, CH*Me$_2$*), 0.68 (dd, 3H, J = 6 Hz, J = 16 Hz, CH*Me$_2$*). ^{13}C{^{1}H} NMR (C_6D_6): δ 230.1 (s, Zr*C*HC$_6$H$_4$Me), 160.1 (dd, J = 2 Hz, J = 24 Hz), 158.7 (dd, J = 3 Hz, J = 20 Hz), 147.0 (s), 134.9(s), 133.0 (s), 132.5, 132.3

(s), 131.4 (s), 131.1 (s), 128.5 (d, $J = 4$ Hz), 128.4 (s), 127.9 (s), 126.0 (s), 123.7 (d, $J = 22$ Hz), 120.7 (d, $J = 7$ Hz), 119.1 (d, $J = 7$ Hz), 116.3 (d, $J = 12$ Hz), 59.1 (s, Zr*C*$H_2C_6H_4$Me), 27.1 (d, $J = 9$ Hz, *C*HMe$_2$), 23.0 (d, $J = 6$ Hz, *C*HMe$_2$), 21.2 (d, $J = 17$ Hz, *C*HMe$_2$), 21.0 (s, Ar-*Me*), 20.9 (d, $J = 10$ Hz, *C*HMe$_2$), 20.9 (s, Ar-*Me*), 20.8 (s, Ar-*Me*), 20.7 (s, Ar-Me), 20.6 (d, $J = 7$ Hz, CH*Me*$_2$), 19.7 (d, $J = 5$ Hz, CH*Me*$_2$), 19.4 (d, $J = 4$ Hz, CH*Me*$_2$), 19.1 (d, $J = 10$ Hz, CH*Me*$_2$), 18.2 (d, $J = 11$ Hz, CH*Me*$_2$), 17.7 (s, CH*Me*$_2$), 15.3 (d, $J = 7$ Hz, CH*Me*$_2$). The remaining CH*Me*$_2$ signal is obscured by the Ar-Me resonances. $^{31}P\{^1H\}$ NMR (C_6D_6): δ 28.4 (d, $J = 58$ Hz), 27.3 (d, $J = 58$ Hz). The selected undecoupled ^{13}C NMR data follow: δ 230.1 (d, $J = 92$ Hz, Zr*C*HC_6H_4Me), 59.0 (t, $J = 132$ Hz, Zr*C*$H_2C_6H_4$Me). The selected ^1H NMR data collected while decoupling the ^{31}P signal at 28.3 ppm follow: 7.10 (d, 1H, $J = 7$ Hz, Ar-*H*), 7.02 (d, 1H, $J = 8$ Hz, Ar-*H*), 2.60 (d, 1H, $J = 9$ Hz, ZrCH_2Ph-*p*-Me), 1.28 (d, 3H, $J = 7$ Hz, CH*Me*$_2$), 1.23 (d, 3H, $J = 7$ Hz, CH*Me*$_2$) 1.16 (d, 3H, $J = 7$ Hz, CH*Me*$_2$), 1.13 (d, 3H, $J = 7$ Hz, CH*Me*$_2$), 0.97 (d, 3H, $J = 7$ Hz, CH*Me*$_2$), 0.89 (d, 3H, $J = 7$ Hz, CH*Me*$_2$), 0.80 (d, 3H, $J = 7$ Hz, CH*Me*$_2$), 0.68 (d, 3H, $J = 7$ Hz, CH*Me*$_2$). Anal. Calcd (Found) for $C_{42}H_{57}NP_2Zr$: C, 69.19 (68.98); H, 7.88 (7.95).

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Supporting Information Available: Experimental details, characterization data, and crystallographic information. This material is available via the Internet free of charge at http://pubs.acs.org.

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