Synthesis and Structure of Group 4 Iminophosphonamide Complexes

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The syntheses of a variety of iminophosphonamide (PN_2) ligands (**2a**−**f**), the corresponding hydrochloride salts (**1a**−**c**), and a number of bis(PN_2) dichloride complexes of group 4 (**3a**−**e**) and their corresponding dialkyls (**5a**−**e**) are described. A novel monosubstituted PN_2 "ate" complex **4** was prepared from ligand **2f** and $Zr(NMe_2)_4$ on treatment with excess $Me_2NH\cdot HCl$. Piano-stool PN_2 zirconium dichloride complexes **6a**−**h** were accessible on treatment of $CpZr(NMe_2)_3$ (Cp = C_5H_5, Cp*) with PN_2 ligands **2a**−**e**, followed by metathesis with excess Me_3SiCl or $Me_2NH\cdot HCl$ (**6a**−**g**) or at low *T* with ethereal HCl (**6h**). Dialkyl derivatives **8a**−**h** could be prepared from **6a**−**h** or directly from ligands **2** and $CpMMe_3$ (Cp = C_5H_5, Cp*; M = Ti or Zr). The intermediate $Cp(PN_2)Zr(NMe_2)_2$, precursor to **6h**, rearranged to the novel terminal difluoride complexes **7a**,**b** at room temperature. A variety of complexes **3** and **6** or their corresponding alkyl derivatives have been characterized by X-ray crystallography. In addition, the novel "ate" complex **4** and difluoride complexes **7a**,**b** have been structurally characterized in this manner. The structures of **7a**,**b** in the solid state reveal strong, intramolecular coordination of the NMe_2 group to the metal center, resulting in eight-coordinate complexes. One of these complexes is fluxional in solution, suggesting rapid exchange of bound versus free NMe_2 groups coupled with the formation of coordination stereoisomers.

Introduction

The synthesis of novel group 4 complexes is of considerable interest in the context of olefin polymerization using "non-metallocene" catalysts.[1] A wide variety of complexes based on the use of surrogates for the Cp ligand have been prepared and many are active in ethylene or α-olefin polymerization. However, the polymerization activities of isoelectronic (or even isolobal) complexes differ dramatically and often in a contradictory manner. Establishing fundamental trends in, for example, catalyst activity with respect to parameters such as total electron count and the steric and electronic effect of ligand substituents has been problematic. These difficulties arise through a number of complicating factors such as the efficiency of activation of catalyst precursors with typical cocatalysts, particularly methyl aluminoxane (PMAO), the stability of the active catalyst (or precatalyst) with respect to irreversible deactivation or reversible inhibition processes, and intrinsic electronic or steric effects on monomer coordination and insertion rates.

Some time ago, a number of workers elected to study group 4 complexes based on the amidinate ligand [$RC(NR')_2 = CN_2$] as catalysts in ethylene or propylene polymerization. This ligand is a hard σ-donor, which can contribute up to 5e ($3\sigma + 2\pi$) on coordination to a d^0 metal.[2] On activation with PMAO in hydrocarbon media, both bis(CN_2)[3] and mixed $Cp(CN_2)$[4] complexes of Ti and Zr were active in ethylene, while the former were also active in propylene polymerization; however, compared with Cp_2ZrX_2 complexes, these 14-electron complexes were approximately 10^2−10^3 times less active under similar conditions of temperature and pressure. Further, some of these complexes [e.g., $Cp(CN_2)ZrCl_2$, R = $SiMe_3$, R′ = Ph] were said to be almost inactive in olefin polymerization;[4a,b] in these cases, thermal instability of cationic alkyls generated in situ from neutral catalyst precursors was believed to be responsible for this finding.

More recently, less-hindered versions of mixed $Cp(CN_2)ZrMe_2$ complexes (Cp = η^5-C_5H_5, η^5-Cp*; R =

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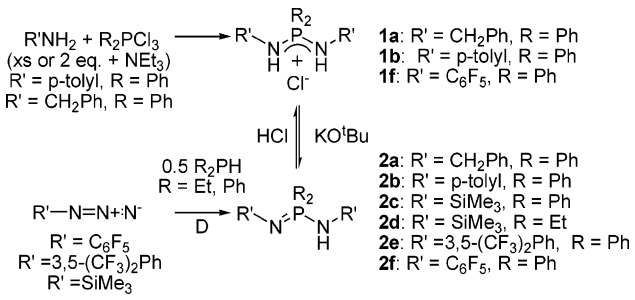
Me and R′ = Et, ^{c}Hx, ^{t}Bu, etc.) have been shown to effect the living polymerization of 1-hexene or other sterically hindered alkenes in chlorobenzene solution on activation with either $[PhNMe_2H][B(C_6F_5)_4]$ or $[Ph_3C][B(C_6F_5)_4]$.[5] Detailed study of these cationic alkyl-Zr complexes has indicated that they are reasonably stable in such media and are less prone to β-H elimination than their Cp_2 counterparts. Further, bimolecular alkyl group exchange processes are facile at higher Zr concentrations[5e,f] and are responsible for erosion of tacticity seen using chiral initiators of this type. Although the polymerization of ethylene or propylene has not been reported in the open literature using these initiators, the activity in hexene polymerization ($\leq 10^5$ g C_6H_{12}/mol Zr × h) suggests that values in the range 10^6-10^7 g monomer/mol Zr × h at 25 °C in this polar solvent are not unlikely.

Several years ago we were intrigued by the origins of the low activities observed for CN_2 complexes of group 4 in ethylene polymerization, at least when activated under conventional conditions using PMAO in hydrocarbon media. We suspected either that the precatalysts were inefficiently activated using PMAO or were insufficiently stable under the conditions studied or that unfavorable steric/electronic effects were at play here. Further, although the CN_2 ligand is sterically demanding with a cone angle comparable to Cp or Cp* depending on substitution,[2] it is an inherently two-dimensional ligand, which might make such complexes more susceptible to bimolecular inhibition and/or degradation processes, compared with their Cp analogues.

We reasoned that a more three-dimensional analogue, such as the iminophosphonamide $[R_2P(NR')_2 = PN_2]$ ligand,[6] where the tetrahedral P(V) atom is thought to represent a minimal electronic perturbation to trigonal C(IV), would be a suitable choice of ligand to investigate such issues. Preliminary work revealed that complexes derived from these ligands had ethylene polymerization activities that rivaled bent metallocene complexes when activated by PMAO under comparable conditions.[7] Herein we report full details for the synthesis of a variety of PN_2 ligands and the synthesis and solid-state structures of group 4 complexes derived from them. In a subsequent paper we will report on the utility of these complexes in ethylene polymerization and their use for living polymerization of hexene.[8]

Scheme 1



Results and Discussion

Synthesis of PN_2 Ligands and PN_2 Complexes. A number of PN_2 complexes of the group 4 metals had been prepared and characterized prior to our work in this area; many of these compounds were synthesized by the reaction of an *N*,*N*,*N*′-tris(trimethylsilyl)-PN_2 ligand with the corresponding titanium or zirconium (IV) chloride.[6] Monosubstituted complexes were generally accessible via this route and were typically dinuclear with halide bridges. In contrast, there were very few reports of disubstituted and no reports of mixed $Cp(PN_2)$ complexes prior to our work. Further, the range of substituents on both P and N in these complexes was rather limited, because of the need for trimethylsilyl chloride elimination as a key step in complex formation.

We thus focused our attention on a more general approach to the synthesis of these complexes and elected to use amine elimination[9] as a complementary route to both mono- and disubstituted PN_2 complexes. Further, we envisaged that the nature of the R and R′ groups on P and N, respectively, would alter the steric and electronic properties of these ligands so that we could study fundamental trends in insertion reactivity with these complexes. Thus, a variety of PN_2 ligands differing in their steric and/or electronic properties were targeted.

As shown in Scheme 1, a variety of NAr-, NR-, or $NSiMe_3$-substituted PN_2 ligands were accessible by one of two established routes. With electron-rich amines or anilines, nucleophilic disubstitution of diphenylphosphoryl trichloride[10] proved expedient (but wasteful of 1° amine) and furnished the corresponding PN_2·HCl salts **1** in high yields. This approach was unsuccessful in the case of electron-deficient anilines such as $C_6F_5NH_2$; in such cases, a complementary method involving the Staüdinger reaction of 2° phosphines with 2 equiv of an aryl- or trimethysilyl-azide[11] proved efficient, affording access to the PN_2 ligands **2** directly. Although the hydrochloride salts **1** are useful reagents in their own right (vide infra), they can be transformed to ligands **2** on treatment with KO^{t}Bu in ether, while the former are accessible from the latter on reaction with anhydrous HCl in ether (as in the case of **1f**). All of these compounds are sensitive toward hydrolysis in solution and are best stored in a glovebox or desiccator under N_2.

The free PN_2 ligands **2** should, in principle, give rise to different sets of NMR signals associated with the

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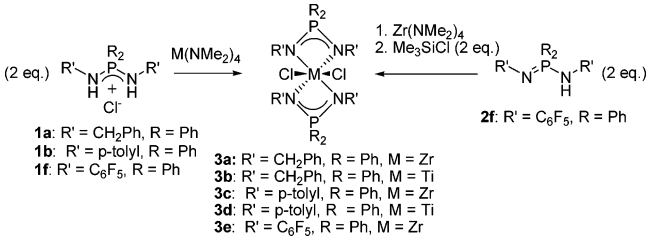
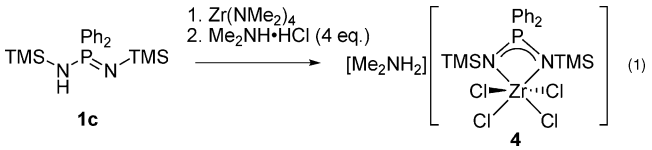
Scheme 2



inequivalent NR moieties in these compounds. In practice this was not usually observed in the ^{1}H NMR spectra of ligands **2a**−**e** at room temperature; however, the ^{19}F NMR spectrum of **2f** clearly showed evidence for fluxional behavior at room temperature, consisting of three line-broadened resonances. On cooling to −60 °C, decoalescence of these into two sets of *o*-, *m*-, and *p*-F resonances was observed. We suspect that rapid exchange of the reasonably acidic N-H proton, in a bimolecular fashion, analogous to the process known for carboxylic acids or amidines,[12] is at play here.

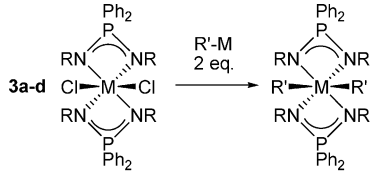
An "atom-economical" route to bis(PN_2) dichloride complexes **3a**−**e** involves direct reaction of hydrochloride salts **1a**,**b** and **1f** with $Zr(NMe_2)_4$ or $Ti(NMe_2)_4$ in a 2:1 ratio (Scheme 2). We suspect these reactions proceed via initial formation of $M(NMe)_2Cl_2$, which has been shown to be a useful starting material in amine elimination reactions.[13] Alternate routes to complexes **3** involved amine elimination reactions of $Zr(NMe_2)_4$ with 2 equiv of the "free" PN_2 ligand **2** to furnish the expected bis(amido)PN_2 complexes in high yield. Generally such intermediates were not isolated but converted to the corresponding dichloride complexes **3** on treatment with either anhydrous $Me_2NH{\cdot}HCl$ or an excess of Me_3SiCl (e.g., synthesis of **3e**, Scheme 2).[14] Although not systematically investigated as a route to monosubstituted PN_2 complexes, the 1:1 reaction of $Zr(NMe)_4$ with PN_2 ligand **2c** cleanly furnished the expected tris(amido) complex; treatment with a 4-fold excess of $Me_2NH{\cdot}HCl$ furnished the novel $[Me_2NH_2][PN_2ZrCl_4]$ complex **4** in variable yield (eq 1). This compound was characterized by X-ray crystallography (vide infra), but its chemistry has not been further studied.



(1)

The dichloride complexes **3** are sensitive to hydrolysis, particularly in solution, but are nicely crystalline and can be readily purified. Their solution ^{1}H, ^{13}C, and, where applicable, ^{19}F NMR spectra are consistent with time-averaged C_{2v} symmetry (see Experimental Section). However, in the solid state, all of these complexes adopt *cis*-quasi-octahedral structures with approximate C_2 symmetry (vide infra). We suspect the higher symmetry observed in solution is due to rapid rotation of these ligands about the P- - -Zr axes, as has been documented for the corresponding amidinate analogues.[3,15]

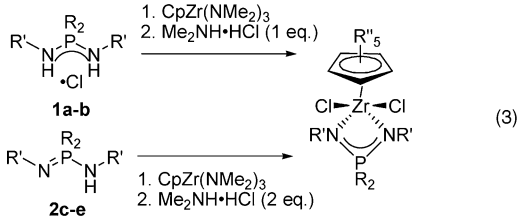
Dimethyl derivatives **5a**−**d** can be readily prepared from dichloride complexes **3** with either MeLi or MeMgBr in ether solution (eq 2). The dibenzyl complex **5e** was prepared from **3c** using 2 equiv of $PhCH_2K$ in toluene suspension. The dialkyls **5** are all readily hydrolyzed but are not pyrophoric; they merely smolder in air. As with their dichloride precursors, complexes **5** exhibit NMR spectra consistent with time-averaged C_{2v} symmetry.



(2)

5a: R = CH_2Ph, R' = Me, M = Zr
5b: R = CH_2Ph, R' = Me, M = Ti
5c: R = p-tolyl, R' = Me, M = Zr
5d: R = p-tolyl, R' = Me, M = Ti
5e: R = p-tolyl, R' = CH_2Ph, M = Zr

Piano-stool, PN_2 zirconium dichloride complexes **6a**−**g** were available through reaction of ligands **2c**−**e** with $CpZr(NMe_2)_3$ [Cp = C_5H_5, C_5Me_5], followed by treatment with either $Me_2NH{\cdot}HCl$ or excess Me_3SiCl (eq 3). In this case, it was also convenient to use salts **1a**,**b** (which are easily purified) even though the intermediate (dimethylamido)chloride complexes had to be converted to the final products **6a**,**b** using the same methods.



(3)

6a: R' = $PhCH_2$, R = Ph, R'' = H
6b: R' = p-tolyl, R = Ph, R'' = H
6c: R' = p-tolyl, R = Ph, R'' = Me
6d: R' = $SiMe_3$, R = Ph, R'' = H
6e: R ' = $SiMe_3$ R = Et, R'' = H
6f: R' = 3,5-$(CF_3)_2$Ph, R = Ph, R'' = H
6g: R' = 3,5-$(CF_3)_2$Ph, R = Ph, R'' = Me

In the case of ligand **2f** (R′ = C_6F_5, R = Ph) amine elimination involving $CpZr(NMe_2)_3$ proceeded in an unexpected manner to give a solid, sparingly soluble in hexane, which is uncharacteristic of these piano-stool bis(amido) complexes. The ^{19}F NMR spectrum of this mixture in C_6D_6 featured multiple resonances in the region δ −100 to −200, characteristic of perfluoroaryl groups, and multiple signals at δ 0 to +100 ppm, some with obvious ^{19}F−^{19}F coupling. The ^{1}H NMR spectrum indicated fluxional behavior for the PPh_2, Cp, and NMe_2 groups and suggested the presence of at least two different compounds based on the Cp region. Crystallization of this material from toluene allowed for sepa-

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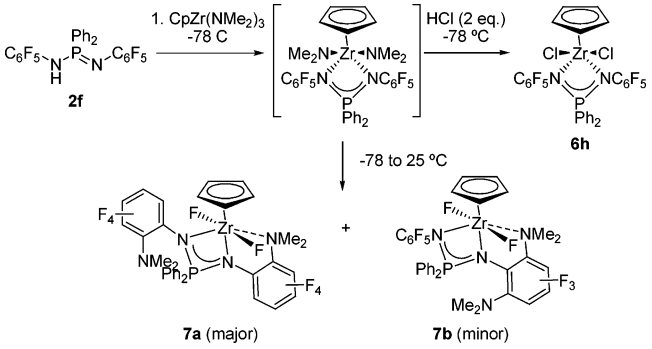
Scheme 3



ration of these compounds, and X-ray structural determinations on both revealed that these compounds were the novel isomeric zirconium difluoride complexes **7a** and **7b** (Scheme 3). The former compound, in which the PN_2 ligand is symmetrically substituted by the *o*-Me_2N-C_6F_4− group, was the major isomer present in the original mixture (ca. 2:1). Evidently, these complexes form via intramolecular, nucleophilic substitution of the C_6F_5 rings at the *o*-position in the putative bis(NMe_2) intermediate, which is unstable at room temperature.[16]

We have been unable to isolate the latter compound under any conditions. Its presence is inferred from the ^{1}H and ^{19}F NMR spectra of a mixture of **2f** and $CpZr(NMe_2)_3$ at low temperature and by the observation that amine elimination, followed by treatment with anhydrous HCl in ether at −78 °C, cleanly furnished the expected dichloride complex **6h** (Scheme 3).

Interestingly, of these two difluoride isomers, only **7a** appears fluxional in solution. The ^{1}H, ^{19}F, and ^{31}P NMR spectra of **7b** were consistent with the static structure shown in Scheme 3 (see Experimental Section). As to the fluxional behavior of **7a**, whose ^{19}F and ^{1}H NMR spectra were variable and complex over the *T* range −80 to +100 °C, we have been unable to completely decipher the nature of the processes responsible for this behavior.

We suspect, based on the X-ray structure which features a dative interaction between one NMe_2 group and the Zr (vide infra), that a combination of reversible, degenerate exchange of bound and free NMe_2 groups, coupled with hindered rotation about the N−Ar bonds or P−Zr axis, is partly responsible for the behavior seen for **7a**. However, there are more than the expected number of terminal F resonances in the ^{19}F NMR spectrum (two sets of doublets with different ^{19}F−^{19}F coupling constants) and two different singlets in the ^{31}P{^{1}H} NMR spectrum of **7a**. This behavior suggests the possibility of coordination stereoisomers (e.g., *cis* versus *trans* fluorides) being present in solution.

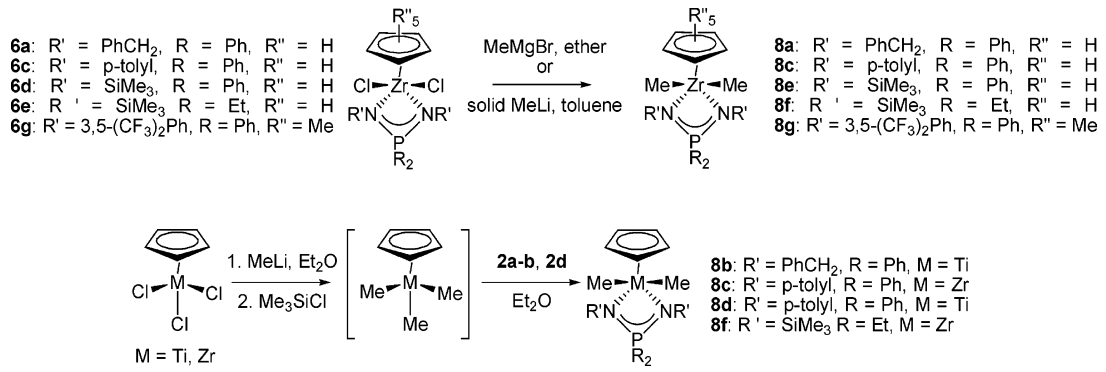
As with their bis(PN_2) counterparts, dialkyl zirconium derivatives **8a**, **8c**, and **8e**−**g** were accessible via conventional reactions with Grignard or organolithium reagents (Scheme 4). However, control of stoichiometry and/or reaction conditions was crucial since in many cases these mixed Zr complexes are susceptible to disproportionation into $(PN_2)_2ZrR_2$ and Cp_2ZrR_2, a process that appears facilitated by an excess (local or otherwise) of R−M (M = MgBr or Li). Similar observations have been made during the synthesis of $Cp(CN_2)$-$ZrMe_2$ complexes via this route.[4a−c,5]

In view of this undesired complexity, a better route to Ti and Zr alkyls **8** was developed; some of these Zr complexes were among the most active in olefin polymerization,[7,8] and gram quantities were needed for mechanistic work in support of these studies.[8] As shown in Scheme 4, reaction of ligands **2a**,**b**, and **2d** with $CpMMe_3$ (Cp = C_5H_5, M = Ti or Zr) cleanly furnished the corresponding alkyls **8b**−**d** and **8f** often in close to quantitative yield. Since the complex $CpZrMe_3$ is unstable in solution above −20 °C,[17] alkane elimination reactions involving the use of this precursor required in situ formation from $CpZrCl_3$ and MeLi prior to the addition of ligands **2**. In these cases it was preferable to use a slight excess of MeLi, to facilitate clean and rapid formation of $CpZrMe_3$, followed by treatment with anhydrous and degassed Me_3SiCl[5] prior to the addition of ligand **2**. This procedure avoided disproportionation of products **8** due the presence of excess MeLi in these mixtures (vide supra).

Structure of PN_2 Complexes. A number of these Ti and Zr complexes have been characterized by X-ray crystallography. The molecular structures of complexes **3a** and **3b**, **5b** and **5e**, **4**, **6b**[7] and **8d**, and **7a** and **7b** appear in Figures 1−5, respectively, while selected crystallographic and refinement data appear in Table 1, and selected metrical parameters appear in Tables 2 and 3, respectively. Full details of these structures are included as Supporting Information. In earlier work, we had also reported the structures of **3c** and **6b**[7] and have included relevant metrical data in Tables 3 and 4 for the sake of comparison and discussion.

The bis(PN_2) dichloride and dialkyl complexes **3** and **5** are characterized by quasi-octahedral geometries featuring *cis* dichloride or dialkyl ligation. These complexes have approximate local C_2 symmetry in the solid state. As would be expected, the M−N distances in the PN_2 ligands track with the identity of both the metal

Scheme 4



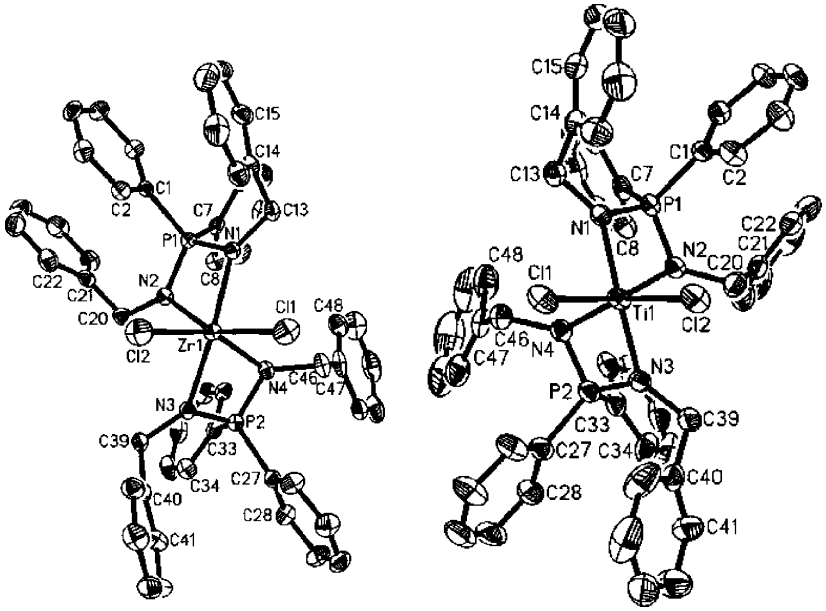


Figure 1. Molecular structures of complexes **3a** and **3b** with 30% thermal ellipsoids depicted and H atoms removed for clarity.

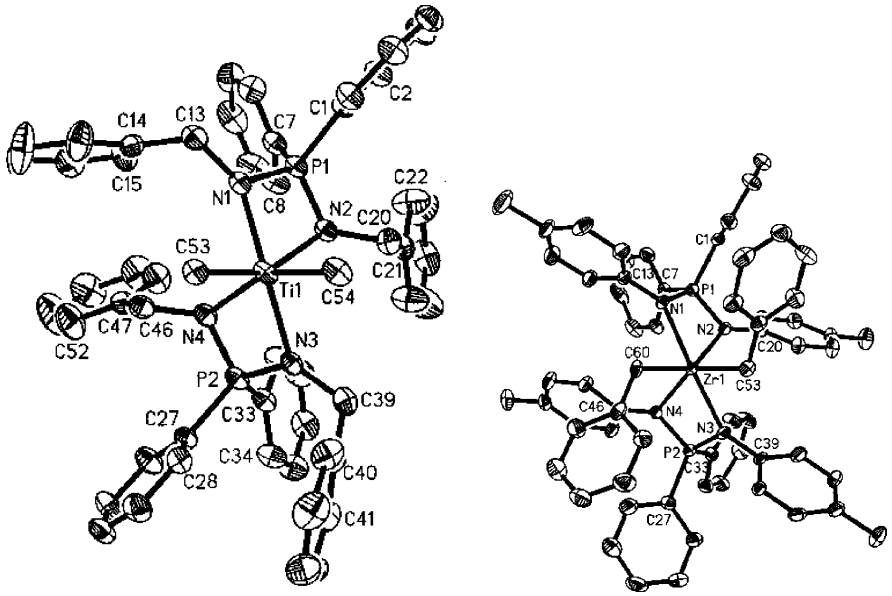


Figure 2. Molecular structures of complexes **5b** and **5e** with 30% thermal ellipsoids depicted and H atoms removed for clarity.

and the nature of the remaining ligands (Table 3), being 2.0−2.7% shorter on average in the case of dichloride complexes **3** relative to the dialkyls **5**. The magnitude of the Ti−N distances [2.031(2)−2.118(2) Å] are 11.0−14.6% shorter on average than the sum of the covalent radii (2.38 Å), while the Zr−N distances [2.174(2)−2.284(2) Å] are only about 2.6% shorter on average than the corresponding distance (2.29 Å). Only the Ti−N bonds could be considered to possess a significant π-component on this basis.

The bite angle of the PN_2 ligand is remarkably consistent over a range of ligands and complexes and is 64.7−66.8(1)° and 69.5−71.5(1)° in the case of Zr and Ti, respectively. There is minor systematic variation of this angle with respect to the remaining ligands, with the angle being about 1.0−1.8(1)° more acute in the case of the dialkyls **5** compared to analogous complexes **3**. The PN distances at 1.600−1.630(2) Å are intermediate between single and double P−N bonds. Again, there is a systematic variation in the P−N bond lengths, being marginally shorter (≤1%) on average in the dialkyls **5** compared with dichloride complexes **3**; interestingly, the P−N distances are essentially independent of the nature of the metal in otherwise identical complexes [e.g., 1.608−1.624(2) versus 1.608−1.628(2) Å for **3b** and **3a**].

There are larger variations in the N−P−N angles in these complexes, being more acute by about 1−2° in the dichlorides versus the dialkyls and by a similar amount for Ti versus Zr. Since the overall variation in this angle is smaller than for the corresponding N−M−N angles

(16) A dimethylamido fluoride complex, a plausible intermediate involved in the formation of **7a** and **7b**, has also been isolated from these mixtures after short reaction times at room temperature and has been characterized spectroscopically. Tomaszewski, R. Unpublished results.

(17) Aitken, C.; Barry, J. P.; Gauvin, F.; Harrod, J. F.; Malek, A.; Rousseau, D. *Organometallics* **1989**, *8*, 1732.

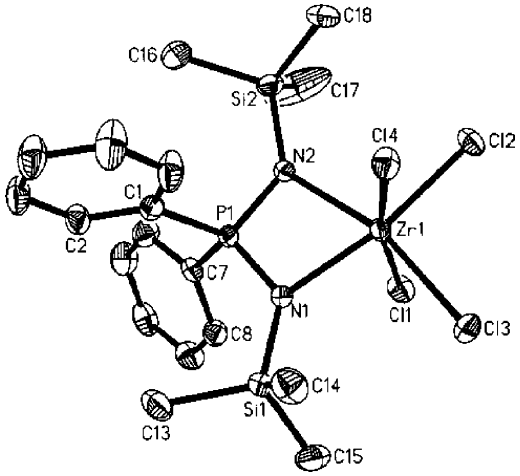


Figure 3. Molecular structure of the anionic portion of "ate" complex **4** with 30% thermal ellipsoids depicted and H atoms removed for clarity.

(ca. 4.4° in the case of **3a** versus **3b**) and these four-membered rings are close to planar (Table 3), the principle effect on changing the metal in these systems is for the PN_2 ligand to simply move farther away from the (larger) metal with a lesser change in the angle at P.

Finally, M−Cl and M−C distances in these structures are within the normal range expected but do show a variation as a function of the M−N distances. Thus, in **3a** the Zr−Cl distances of 2.466(1) and 2.478(1) Å are about 2% longer than in **3c** [2.436(1) and 2.431(1) Å], which mirrors the variation seen in the corresponding M−N distances (longer on average for **3c**). The angle defined by the metal and these two remaining ligands varies from 86.5(1)° to 95.7(1)° with $TiMe_2$ and $ZrCl_2$ angles being at the lower and upper ranges, respectively. The angle between these two ligands appears to be independent of the metal as the R−M−R angles are 4.35(7)−4.4(1)° more acute than the corresponding Cl−M−Cl angles for both Ti and Zr. Overall, the structures of the Zr complexes are analogous to structurally characterized bis(CN_2) complexes featuring alkyl/aryl substitution on N,[3,18] the differences mainly evident in the more acute bite angle of the CN_2 ligand and the somewhat shorter M−N distances in the case of the PN_2 complexes.

A curious feature is evident in the structures of the N-benzyl Ti complexes **3b** and **5b**. Namely, the geometry at N(2) and N(4) is distorted from trigonal planar toward tetrahedral. In the case of complex **3b** the sum of the angles about N(2) and N(4) respectively are 349.6(1)° and 350.5(1)°, while the corresponding values for complex **5b** are 349.8(1)° and 349.5(1)°, respectively. At first this distortion was attributed to possible H-bonding between the N-CH_2Ph protons and the chloride

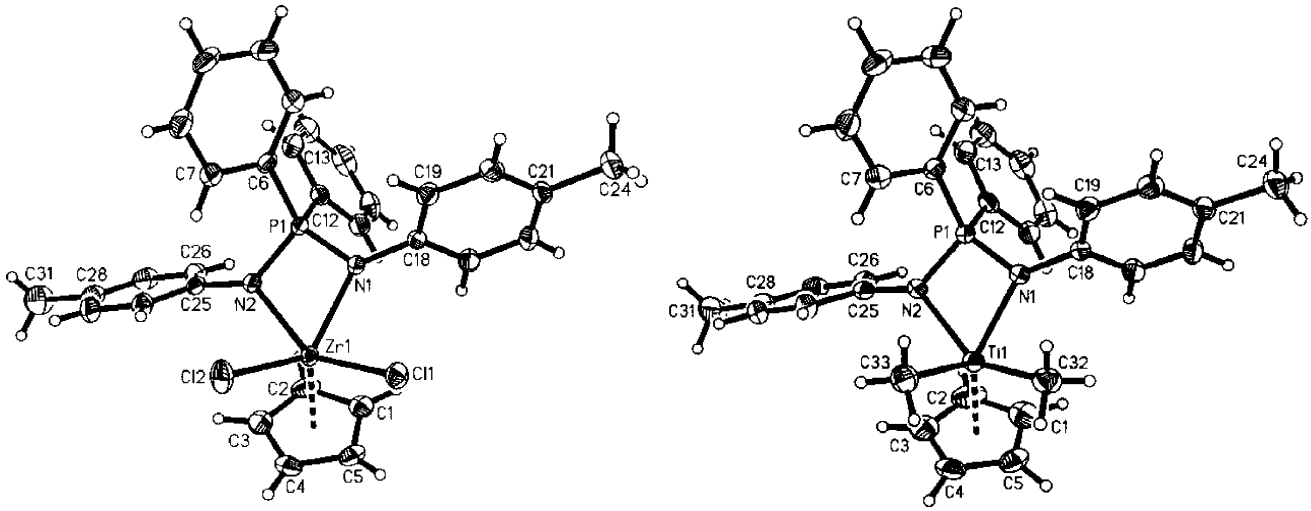


Figure 4. Molecular structures of complexes **6b**[7] and **8d** with 30% thermal ellipsoids depicted.

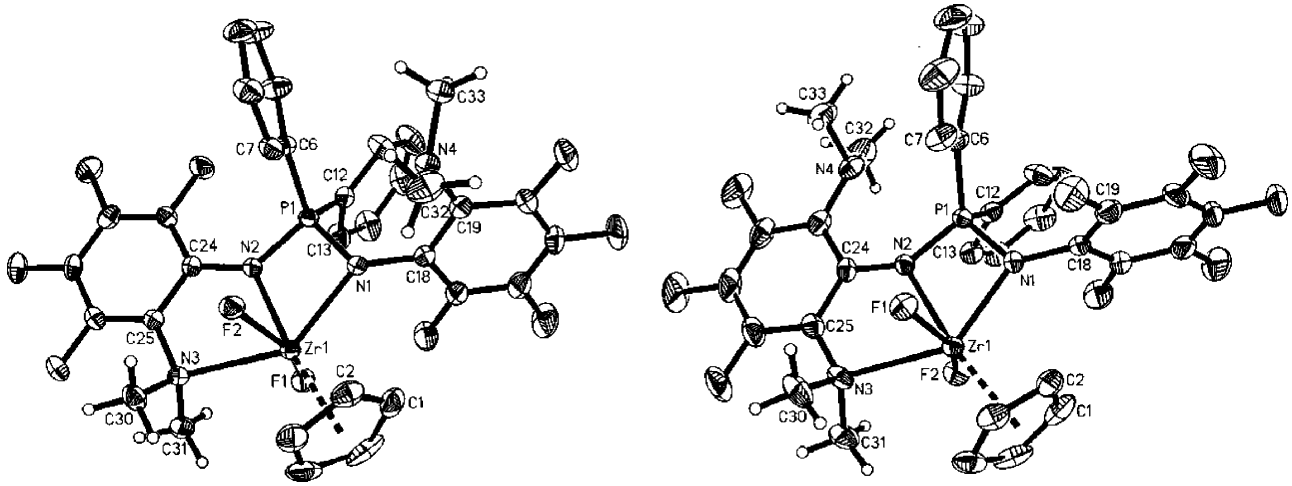


Figure 5. Molecular structures of complexes **7a** and **7b** with 30% thermal ellipsoids depicted and selected H atoms depicted.

Table 1. Selected Crystallographic and Refinement Data for PN_2 Complexes[a]

	3a	**3b**	**4**	**5b**
emp formula	$C_{52}H_{48}Cl_2N_4P_2Zr$	$C_{52}H_{48}Cl_2N_4P_2Ti$	$C_{20}H_{36}Cl_4N_3PSi_2Zr$	$C_{53.85}H_{53.55}Cl_{0.15}N_4P_2Ti$[b]
fw	953.00	909.68	638.69	871.91
cryst syst	monoclinic	monoclinic	monoclinic	orthorhombic
space group	*P*2(1)/*c*	*P*2(1)/*c*	*P*2(1)/*n*	*Pbca*
unit cell (Å and deg)	*a* = 10.265(3), α = 90	*a* = 10.605(1), α = 90	*a* = 9.1834(9), α = 90	*a* = 20.360(3), α = 90°
	b = 21.493(4), *β* = 93.02(1)	*b* = 21.317(2), *β* = 90.32(1)	*b* = 16.569(1), *β* = 90.54(1)	*b* = 20.087(2), *β* = 90°
	c = 20.721(4) *γ* = 90	c = 20.485(2), *γ* = 90	c = 20.171(2), *γ* = 90	c = 22.375(2), *γ* = 90°
volume (Å^3)	4565(2)	4630.9(8)	3069.1(5)	9151(2)
Z	4	4	4	8
ρ(calcd) (Mg/m^3)	1.387	1.305	1.382	1.266
abs coeff (mm^{-1})	0.469	0.410	0.850	0.307
F(000)	1968	1896	1312	3674
cryst size (mm^3)	0.42 × 0.37 × 0.34	0.54 × 0.52 × 0.52	0.56 × 0.36 × 0.21	0.96 × 0.60 × 0.60
θ range (deg)	2.14−25.00	2.14−25.00	2.36−25.00	2.00−27.00
no. of reflns coll	8519	8606	5752	9952
no. of indep reflns	8040 [*R*(int) = 0.0227]	8138 [*R*(int) = 0.0157]	5394 [*R*(int) = 0.0123]	9952
max./min. transmn	0.874/0.846	0.833/0.814	0.846/0.741	0.847/0.762
no. of data/params	8040/551	8138/550	5394/289	9952/550
GOF (*F*^{2})	1.696	2.617	1.823	2.254
R indices [*I*>2*σ*(*I*)]	R1 = 0.0295 wR2 = 0.0602	R1 = 0.0357 wR2 = 0.0735	R1 = 0.0214 wR2 = 0.0497	R1 = 0.0421 wR2 = 0.0906
R indices (all data)	R1 = 0.0390 wR2 = 0.0610	R1 = 0.0435 wR2 = 0.0738	R1 = 0.0251 wR2 = 0.0500	R1 = 0.0569 wR2 = 0.0914

	5e	**7a**	**7b**	**8d**
emp formula	$C_{80}H_{78}N_4P_2Zr$	$C_{33}H_{27}F_{10}N_4PZr$	$C_{39.70}H_{34.10}Cl_{0.30}F_{10}N_4PZr$[c]	$C_{33}H_{35}N_2PTi$
fw	1248.62	791.78	890.03	538.50
cryst syst	monoclinic	triclinic	monoclinic	monoclinic
space group	*Pn*[d]	*P*$\bar{1}$	*P*2(1)/*c*	*P*2(1)/*c*
unit cell (Å and deg)	*a* = 17.346(2), α = 90	*a* = 9.946(1), α = 97.45(1)	*a* = 15.074(1), α = 90	*a* = 8.998(1), α = 90
	b = 10.437(1), *β* =103.93(1)	*b* = 12.725(2), *β* = 102.87(1)	*b* = 11.865(1), *β* = 101.42(1)	*b* = 25.879(2), *β* = 97.86(1)
	c = 18.653(2), *γ* = 90	*c* = 12.947(1), *γ* = 90.50(1)	*c* = 21.633(2), *γ* = 90	*c* = 12.215(1), *γ* = 90
volume (Å^3)	3277.7(6)	1582.7(3)	3792.6(6)	2817.7(4)
Z	2	2	4	4
ρ(calcd) (Mg/m^3)	1.265	1.661	1.559	1.269
abs coeff (mm^{-1})	0.265	0.489	0.438	0.385
F(000)	1312	796	1802	1136
cryst size (mm^3)	0.74 × 0.52 × 0.36	0.42 × 0.26 × 0.20	0.74 × 0.70 × 0.38	0.70 × 0.36 × 0.36
θ range (deg)	2.25−25.00	2.10−26.00	2.13−28.00	2.28−28.00
no. of reflns coll	5964	6592	9459	7210
no. of indep reflns	5964	6214 [*R*(int) = 0.0177]	9126 [*R*(int) = 0.0131]	6804 [*R*(int) = 0.0135]
max./min. transmn	0.915/0.874	0.914/0.880	0.856/0.750	0.886/0.863
no. of data/params	5964/787	6214/447	9126/507	6804/338
GOF (on *F*^{2})	2.165	1.545	2.116	1.940
R indices [*I*>2*σ*(*I*)]	R1 = 0.0261 wR2 = 0.0631	R1 = 0.0248 wR2 = 0.0509	R1 = 0.0321 wR2 = 0.0898	R1 = 0.0343 wR2 = 0.0681
R indices (all data)	R1 = 0.0275 wR2 = 0.0633	R1 = 0.0318 wR2 = 0.0515	R1 = 0.0400 wR2 = 0.0905	R1 = 0.0463 wR2 = 0.0689

[a] All data were collected at 160 K using graphite-monochromated Mo Kα radiation (*λ* = 0.71073 Å) and a Siemens P4 diffractometer using *ω* scans. Unit cell parameters were determined from 25 general reflections well distributed in reciprocal space. Crystal stability was monitored every 100 reflections. Structure solution and refinement was by Patterson and Fourier techniques with full-matrix least-squares refinement on *F*^{2}. Full details of the structures are included as Supporting Information. [b] Structure was disordered and could be fit to a model in which 15% of the Ti−C(54) sites were disordered with a Ti−Cl(54) atom; see Supporting Information. [c] The structure featured a disordered toluene molecule that could be modeled by inclusion of chlorobenzene at 30% occupancy; see Supporting Information. [d] Flack parameter = 0.00(14).

ligands in **3b**, as the former were oriented toward the latter in the solid-state structure. However, this same distortion from planarity at N was also seen in the dialkyl complex **5b** and is of a similar magnitude.

Since there are no obvious inter- or intramolecular contacts that might sterically distort these N-benzyl substituents, we have to attribute this tendency toward pyramidalization as intrinsic. Tentatively, delocalization of lone pair electron density through P (or Ti) would appear to be less effective in these N-alkyl (versus N-aryl) Ti complexes. Although the P−N and M−N bond lengths show differences (which are longer in the N−Bn complexes) consistent with this interpretation, it should

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Table 2. Selected Bond Lengths and Angles for Bis(PN_2) Complexes

3a		**3b**		**3c**[7]		**5b**		**5e**	
				Bond Lengths [Å]					
Zr(1)−N(1)	2.174(2)	Ti(1)−N(3)	2.031(2)	Zr(1)−N(1)	2.198(2)	Ti(1)−N(1)	2.090(2)	Zr(1)−N(2)	2.242(4)
Zr(1)−N(2)	2.180(2)	Ti(1)−N(1)	2.033(2)	Zr(1)−N(2)	2.237(2)	Ti(1)−N(4)	2.104(2)	Zr(1)−N(3)	2.254(3)
Zr(1)−N(3)	2.188(2)	Ti(1)−N(2)	2.056(2)	Zr(1)−N(3)	2.226(2)	Ti(1)−N(3)	2.106(2)	Zr(1)−N(4)	2.262(3)
Zr(1)−N(4)	2.191(2)	Ti(1)−N(4)	2.064(2)	Zr(1)−N(4)	2.223(2)	Ti(1)−N(2)	2.118(2)	Zr(1)−N(1)	2.284(3)
Zr(1)−Cl(1)	2.466(1)	Ti(1)−Cl(1)	2.362(1)	Zr(1)−Cl(1)	2.436(1)	Ti(1)−C(53)	2.179(2)	Zr(1)−C(60)	2.312(4)
Zr(1)−Cl(2)	2.478(1)	Ti(1)−Cl(2)	2.368(1)	Zr(1)−Cl(2)	2.431(1)	Ti(1)−C(54)	2.179[a]	Zr(1)−C(53)	2.313(4)
						Ti(1)−Cl(54)	2.367[a]		
P(1)−N(2)	1.610(2)	P(1)−N(2)	1.612(2)	P(1)−N(2)	1.628(2)	P(1)−N(2)	1.600(2)	P(1)−N(1)	1.618(4)
P(1)−N(1)	1.628(2)	P(1)−N(1)	1.624(2)	P(1)−N(1)	1.630(2)	P(1)−N(1)	1.606(2)	P(1)−N(2)	1.619(3)
P(2)−N(4)	1.608(2)	P(2)−N(4)	1.608(2)	P(2)−N(4)	1.622(2)	P(2)−N(4)	1.601(2)	P(2)−N(3)	1.605(4)
P(2)−N(3)	1.617(2)	P(2)−N(3)	1.624(2)	P(2)−N(3)	1.626(3)	P(2)−N(3)	1.608(2)	P(2)−N(4)	1.623(3)
				Bond Angles [deg]					
N(1)−Zr(1)−N(2)	66.8(1)	N(1)−Ti−N(2)	71.2(1)	N(1)−Zr(1)−N(2)	65.8(1)	N(4)−Ti(1)−N(3)	69.6(1)	N(3)−Zr(1)−N(4)	64.7(1)
N(3)−Zr(1)−N(4)	67.2(1)	N(3)−Ti−N(4)	71.5(1)	N(3)−Zr(1)−N(4)	65.7(1)	N(1)−Ti(1)−N(2)	69.5(1)	N(2)−Zr(1)−N(1)	64.8(1)
Cl(1)−Zr−Cl(2)	93.34(2)	Cl(1)−Ti−Cl(2)	90.84(2)	Cl(1)−Zr−Cl(2)	95.7(1)	C(54)−Ti−C(53)	86.5(1)	C(60)−Zr−C(53)	91.3(1)
N(2)−P(1)−N(1)	95.4(1)	N(2)−P(1)−N(1)	94.8(1)	N(2)−P(1)−N(1)	95.4(1)	N(2)−P(1)−N(1)	96.9(1)	N(1)−P(1)−N(2)	97.0(2)
N(4)−P(2)−N(3)	97.4(1)	N(4)−P(2)−N(3)	95.5(1)	N(4)−P(2)−N(3)	96.0(1)	N(4)−P(2)−N(3)	96.9(1)	N(3)−P(2)−N(4)	97.0(2)
Σ∠N(1)[b]	360.0(1)	Σ∠N(1)[b]	359.7(2)	Σ∠N(1)[b]	360.0(2)	Σ∠N(1)[b]	359.1(1)	Σ∠N(1)[b]	358.2(3)
Σ∠N(2)[b]	359.9(1)	Σ∠N(2)[b]	349.6(1)	Σ∠N(2)[b]	358.4(2)	Σ∠N(2)[b]	349.8(1)	Σ∠N(2)[b]	360.0(3)
Σ∠N(3)[b]	358.9(1)	Σ∠N(3)[b]	359.1(2)	Σ∠N(3)[b]	360.0(2)	Σ∠N(3)[b]	358.6(1)	Σ∠N(3)[b]	359.8(3)
Σ∠N(4)[b]	351.6(2)	Σ∠N(4)[b]	350.5(1)	Σ∠N(4)[b]	359.6(2)	Σ∠N(4)[b]	349.5(1)	Σ∠N(4)[b]	360.0(3)
Σ∠P(1)N_2Zr[c]	360.0(1)	Σ∠P(1)N_2Ti[c]	360.0(1)	Σ∠P(1)N_2Zr[c]	359.9(1)	Σ∠P(1)N_2Ti[c]	359.8(1)	Σ∠P(1)N_2Zr[c]	358.9(2)
Σ∠P(2)N_2Zr[c]	360.0(1)	Σ∠P(2)N_2Ti[c]	360.0(1)	Σ∠P(2)N_2Zr[c]	360.0(1)	Σ∠P(2)N_2Ti[c]	360.0(1)	Σ∠P(2)N_2Zr[c]	359.8 (2)

[a] C(54) is site-disordered with about 15% of Cl(54) arising from an impurity in the lattice, and neither atom's position was refined. [b] Sum of the endo- and exo-cyclic bond angles about N(1), N(2), N(3), and N(4), respectively. [c] Sum of the angles within the PN_2M rings.

Table 3. Selected Bond Lengths and Angles for Complex 4 and Cp(PN_2)MX_2 Complexes

4		**6c**[7]		**7a**		**7b**		**8d**	
				Bond Lengths [Å]					
Zr(1)−N(1)	2.176(1)	Zr(1)−N(1)	2.186(2)	Zr(1)−N(1)	2.235(1)	Zr(1)−N(1)	2.198(2)	Ti(1)−N(1)	2.109(1)
Zr(1)−N(2)	2.178(2)	Zr(1)−N(2)	2.215(1)	Zr(1)−N(2)	2.236(1)	Zr(1)−N(2)	2.251(2)	Ti(1)−N(2)	2.156(1)
Zr(1)−Cl(4)	2.478(1)	Zr(1)−Cl(1)	2.450(1)	Zr(1)−F(1)	1.972(1)	Zr(1)−F(2)	1.987(1)	Ti(1)−C(32)	2.159(2)
Zr(1)−Cl(2)	2.478(1)	Zr(1)−Cl(2)	2.429(1)	Zr(1)−F(2)	1.993(1)	Zr(1)−F(1)	1.990(1)	Ti(1)−C(33)	2.124(2)
Zr(1)−Cl(1)	2.486(1)	Zr(1)−C(1)	2.471(2)	Zr(1)−N(3)	2.525(2)	Zr(1)−N(3)	2.483(2)	Ti(1)−C(1)	2.349(2)
Zr(1)−Cl(3)	2.493(1)	Zr(1)−C(2)	2.492(2)	Zr(1)−C(1)	2.528(2)	Zr(1)−C(1)	2.525(2)	Ti(1)−C(2)	2.365(2)
P(1)−N(1)	1.618(2)	Zr(1)−C(5)	2.502(2)	Zr(1)−C(5)	2.553(2)	Zr(1)−C(2)	2.527(2)	Ti(1)−C(5)	2.37(2)
P(1)−N(2)	1.620(2)	Zr(1)−C(3)	2.513(2)	Zr(1)−C(2)	2.555(2)	Zr(1)−C(4)	2.553(2)	Ti(1)−C(3)	2.386(2)
		Zr(1)−C(4)	2.535(2)	Zr(1)−C(4)	2.556(2)	Zr(1)−C(5)	2.556(2)	Ti(1)−C(4)	2.399(2)
		P(1)−N(1)	1.619(1)	Zr(1)−C(3)	2.579(2)	Zr(1)−C(3)	2.570(2)	Ti(1)−X1A	2.057(2)
		P(1)−N(2)	1.616(1)	Zr(1)−X1A	2.236(2)	Zr(1)−X1A	2.250(2)	P(1)−N(2)	1.603(1)
				P(1)−N(2)	1.610(2)	P(1)−N(2)	1.598(2)	P(1)−N(1)	1.609(1)
				P(1)−N(1)	1.637(2)	P(1)−N(1)	1.647(2)		
				Bond Angles [deg]					
N(1)−Zr(1)−N(2)	69.6(1)	N(1)−Zr(1)−N(2)	65.9(1)	N(1)−Zr(1)−N(2)	65.1(1)	N(1)−Zr(1)−N(2)	64.8(1)	N(1)−Ti(1)−N(2)	68.2(1)
Cl(2)−Zr−Cl(3)	99.20(2)	Cl(1)−Zr(1)−Cl(2)	91.8(1)	N(2)−Zr(1)−N(3)	71.4(1)	N(2)−Zr(1)−N(3)	71.0(1)	C(33)−Ti−C(32)	85.9(1)
Cl(4)−Zr−Cl(1)	168.70(2)	N(2)−P(1)−N(1)	95.5(1)	F(1)−Zr(1)−F(2)	151.1(1)	F(2)−Zr(1)−F(1)	151.4(1)	N(2)−P(1)−N(1)	96.2(1)
				N(2)−P(1)−N(1)	95.6(1)	N(2)−P(1)−N(1)	94.6(1)		
Σ∠N(1)[a]	359.6(1)	Σ∠N(1)[a]	359.8(1)	Σ∠N(1)[a]	354.6(1)	Σ∠N(1)[a]	359.2(1)	Σ∠N(1)[a]	359.6(1)
Σ∠N(2)[a]	359.8(1)	Σ∠N(2)[a]	359.6(1)	Σ∠N(2)[a]	358.0(1)	Σ∠N(2)[a]	359.1(1)	Σ∠N(2)[a]	358.5(2)
Σ∠ZrN_2P[b]	359.8(1)	Σ∠ZrN_2P[b]	359.8(1)	Σ∠ZrN_2P[b]	359.6(1)	Σ∠ZrN_2P[b]	359.8(1)	Σ∠TiN_2P[b]	360.0(1)
				Σ∠ZrN_2C_2[c]	539.3(2)	Σ∠ZrN_2C_2[c]	539.7(2)		
				Σ∠ZrN_3X1A[d]	359.9(2)	Σ∠ZrN_3X1A[d]	360.0(2)		

[a] Sum of the endo- and exo-cyclic angles around N(1) and N(2), respectively. [b] Sum of the angles within the PN_2M ring. [c] Sum of the angles with the five-membered ring defined by Zr(1), N(1), C(24), C(25), and N(3). [d] Sum of the angles around Zr(1) involving the atoms N(1), N(2), N(3), and the metal centroid X1A.

be noted that the differing hybridization of the exocyclic N−R bonds could also lead to such behavior.

In the case of the unique structure of **4**, which features a PN_2 ligand substituted by N-TMS groups, the structure differs somewhat from those reported earlier.[6] The zirconium atom is octahedrally coordinated with two axial and two equatorial chloride ligands. Given that **4** is actually an "ate" complex, in which the dimethylammonium counterion is H-bonded to one of the axial chloride ligands,[19] it is not surprising that the Zr−N bond lengths are somewhat longer than in otherwise analogous neutral chloride complexes. Further, the PN_2 bite angle is narrowed because of this distortion, while the remaining metrical parameters associated with the PN_2 ligand are similar to PN_2Zr compounds first characterized by Roesky and coworkers.[6]

The mixed ligand Cp(PN_2) complexes **6b**[7] and **8d** feature structures similar to their bis(PN_2) complexes as far as the PN_2 ligand is concerned. On average, the M−N distances are slightly longer in the mixed complexes when compared to their bis(PN_2) analogues. Similarly, the bite angles of the PN_2 ligands are somewhat narrower here compared with the corre-

(19) See Supporting Information for details of this structure.

sponding bis(PN_2) complexes. The metal−Cp distances are typical for these piano-stool complexes,[20] and the only significant distortion from the expected four-legged piano-stool geometry is the twisting of the PN_2 ligand with respect to the plane defined by the metal centroid, the metal, and the bisector of the MX_2 angle. The frontier orbitals in a $CpMX_2$ fragment[21] are such that maximal π-donation from N to M is possible from an orientation where the PN_2 ligand is orthogonal to this plane. Since the M−N bond distances do not imply significant π-donation, it is possible that the skewed arrangements seen reflect a low-energy barrier to rotation about the M- - -P axis. Similar effects have been noted in neutral amidinate complexes of this type.[4,15]

The structures of **7a** and **7b** deserve special comment. A basic structural motif is common to both isomers and which can be thought of as a quasi-octahedral geometry with the Cp ligand occupying a single vertex, even though this ligand is normally considered three-coordinate. In particular, the sum of the angles about the metal defined by the metal−centroid and the three N atoms is 360° within experimental error (Table 3), while the *trans* F atoms are distorted away from the Cp ligand toward the less sterically encumbered PN_2 ligand. The latter tridentate ligand adopts a *mer* relationship with the metal in both structures and in which both the N(1)−P(1)−N(2)−M and N(2)−C(24)−C(25)−N(3)−M rings are planar within experimental error (Table 3). The P(1)−N(1) and P(1)−N(2) distances are marginally dissimilar, while the Zr−N distances show considerable variation, and as might be expected, the dative Zr(1)−N(3) distances are much longer than the other two remaining Zr−N bonds. The Zr−F distances in these structures are short but are of comparable length to those found in other metallocene complexes bearing terminal Zr−F bonds.[22]

Conclusions

A wide variety of bis(PN_2) and mixed Cp(PN_2) complexes of group 4 are available by amine elimination reactions and the corresponding PN_2 ligands **2** or their hydrochloride salts **1**. The synthetic routes to these ligands allow for considerable latitude as to the steric and electronic nature of the substituents on N or P in the resulting complexes. The solid-state structures of complexes **3**−**8** show that they are similar to amidinate complexes that have been characterized, the principle differences revolving around the more obtuse bite angle of the PN_2 ligand and marginally shorter M−N bond lengths. Overall, the structures of these complexes are consistent with the PN_2 ligand functioning as a 3e donor with a minimal π-component to the M−N bonding, and thus these complexes should be considered as 14- rather than 16-electron complexes. The full details concerning olefin polymerization and allied chemistry of this class of compounds will reported in due course.[8]

Experimental Section

All reactions were conducted under an atmosphere of dry N_2. Standard techniques for the manipulation of air-sensitive compounds were employed.[23] All solvents were reagent grade and were purified using a solvent purification system similar to that described in the literature.[24] The following chemicals were obtained from commercial sources and used without further purification unless otherwise noted: Ph_2PCl, MeLi (1.4 M in Et_2O, titrated with 1,3-diphenylacetone-*p*-tosylhydrozone[25]). The compounds $Zr(NMe_2)_4$,[9] $CpZr(NMe_2)_3$,[26] $Cp^*Zr(NMe_2)_3$,[26] Cp^*ZrMe_3,[27] Ph_2PCl_3,[28] C_6F_5-N_3,[29] and 3,5-$(CF_3)_2C_6H_3$-N_3[30] were prepared according to literature methods.

^1H and ^{13}C NMR spectra (referenced to residual protonated solvent) were recorded on a Bruker AC 200, AM 250, or AC 300 or Varian Innova 400 MHz spectrometer. Chemical shifts are referenced to residual undeutrated solvent. ^{31}P NMR spectra (referenced to external 85% H_3PO_4) and ^{19}F NMR spectra (referenced to external $CFCl_3$) were obtained in the solvent indicated on a Bruker AC 200 or Varian Innova 400 MHz spectrometer. IR spectra were recorded on a Bomem MB100 FT-IR instrument. Elemental analyses were performed by Oneida Research Services, NY.

Solid Methyllithium. An Aldrich SureSeal bottle was opened up and the MeLi solution removed. About 90% of the solvent was removed in vacuo, and then hexanes (50 mL) was added to cause the precipitation of a large amount of white solid. This process (reducing the volume and then adding hexanes) was repeated two more times and then the slurry pumped to dryness. ^1H NMR spectroscopy showed that there was a small amount of residual Et_2O (less than 1%), but that the only other proton source was MeLi. From later reactions it became apparent that the solid contains only 69 mol % MeLi. The residual solid is most likely LiCl.

Diphenyl(benzylamino)(benzylimino)phosphorane Hydrochloride, 1a. In a typical reaction, Ph_2PCl_3 (5.00 g, 17.1 mmol) was placed in a Schlenk flask with CH_2Cl_2 (200 mL). The solution was cooled to 0 °C, and the appropriate amine was added over about 30−60 min ($BzNH_2$ (7.49 mL, 68.6 mmol, d = 0.981)). During addition, a large amount of white solid (identified as RNH_3Cl) precipitated. Once the addition was complete, the solution was refluxed overnight to ensure complete reaction. After 12 h, the solution was filtered in the air and the filtrate pumped to dryness. The resulting white solid was recrystallized from CH_2Cl_2/hexanes. Often this did not result in a solid but in a large quantity of oil that was easily separated. Residual solvent can be removed by heating overnight in vacuo to give a white crystalline solid (6.65 g, 89%). Spectral data were virtually identical with the corre-

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sponding compounds reported by Garcia and Cristau.[10] ^{1}H NMR ($CDCl_3$): δ 7.94−7.89 and 7.43−7.04 (br m, 21 H, C_6H_5 and N*H*), 3.97 (dd, 4H, CH_2Ph, $^3J_{PH}$ = 13 Hz, $^2J_{HH}$ = 7 Hz). ^{31}P NMR (CH_2Cl_2): δ 38.3. Anal. Calcd for $C_{26}H_{26}PN_2Cl$: C, 72.13; H, 6.05; N, 6.47. Found: C, 71.57; H, 6.11; N, 6.13.

Diphenyl(*p*-tolylamino)(*p*-tolylimino)phosphorane Hydrochloride, 1b. A solution of *p*-tolylNH_2 (14.7 g, 137 mmol) in CH_2Cl_2 (100 mL) was added to a solution of Ph_2PCl_3 (10.000 g, 34.3 mmol) in CH_2Cl_2 (200 mL). The reaction was worked up in a manner similar to that described above for the preparation of **1a**. This resulted in a white powder (14.22 g, 96%). ^{1}H NMR ($CDCl_3$): δ 9.79 (d, 1H, N*H*, $^3J_{PH}$ = 11 Hz), 8.07−7.99 and 7.52−7.27 (br m, 10H, C_6H_5), 7.18 and 6.69 (AB doublets, 8H, $C_6H_4CH_3$, $^3J_{HH}$ = 8.0 Hz), 2.06 (s, 6 H, $C_6H_4CH_3$). ^{31}P NMR (CH_2Cl_2): δ 28.0. Anal. Calcd for $C_{26}H_{26}PN_2Cl$: C, 72.13; H, 6.05; N, 6.47. Found: C, 72.27; H, 6.20; N, 6.18.

Diphenyl(benzylamino)(benzylimino)phosphorane, 2a. A solution of **1a** (3.00 g, 6.94 mmol) in 100 mL of dry CH_2Cl_2 was placed in a 500 mL Schlenk flask under N_2 and cooled to 0 °C in an ice bath. A diethyl ether solution of potassium *tert*-butoxide (0.79 g, 7.0 mmol) was added to the flask by cannula. The reaction mixture was stirred for 5 min, and the volatiles were removed under vacuum. The remaining solid was extracted with toluene. Removal of toluene from the extract afforded a white solid, which was further purified by recrystallization from toluene and hexane. Yield: 2.2 g (5.6 mmol, 81%). ^{1}H NMR ($CDCl_3$): δ 7.9−7.2 (20H, aromatic protons), 4.22 (d, 4H, NCH_2Ph, $^3J_{PH}$ = 14.0 Hz). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 132.2, 132.0, 131.2, 128.6, 127.5, 126.4 (aromatic carbons), 46.1 (N*C*H$_2$Ph). ^{31}P{^{1}H} NMR (CH_2Cl_2): δ 11.4. Anal. Calcd for $C_{26}H_{25}PN_2$: C, 78.77; H, 6.36; N, 7.07. Found: C, 79.00; H, 6.37; N, 6.86.

Diphenyl(*p*-tolylamino)(*p*-tolylimino)phosphorane, 2b. Method A. To a 500 mL Erlenmeyer flask was added 150 mL of a CH_2Cl_2 solution of **1b** (5.00 g, 11.6 mmol) and 100 mL of 3% KOH aqueous solution. The mixture was vigorously stirred for 5 min, and the CH_2Cl_2 layer was then separated. The aqueous layer was extracted with CH_2Cl_2 (2 × 50 mL). The extract was combined and dried over anhydrous $MgSO_4$. Filtration and removal of CH_2Cl_2 in a vacuum afforded free ligand as a white crystalline solid. Yield: 4.50 g (11.4 mmol, 98%). ^{1}H NMR ($CDCl_3$): δ 7.93, 7.42, 6.94 (18H, aromatic protons), 5.31 (s, 1H, N*H*), 2.21 (s, 6H, NPhCH_3).

Method B. Compound **1b** (2.00 g, 4.6 mmol) was placed in a Schlenk flask with KO^{t}Bu (520 mg, 4.6 mmol), ether (30 mL) was added, and the mixture was allowed to stir for 1 h. The resulting solution was filtered through Celite, and the filtrate was reduced to dryness to produce a white solid (1.59 g, 87%). ^{1}H NMR (C_6D_6): δ 8.01−7.93 and 7.15−6.86 (br m, 18H, C_6H_5 and $C_6H_4CH_3$), 4.85 (br s, 1H, N*H*), 2.06 (s, 6H, $C_6H_4CH_3$). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 132.7, 132.0, 131.9, 131.7, 129.7, 129.9, 128.7, 120.9 (*C*$_6$H$_5$ and *C*$_6$H$_4$CH$_3$), 20.6 ($C_6H_4CH_3$). ^{31}P NMR (CH_2Cl_2): δ 22.3. Anal. Calcd for $C_{26}H_{25}PN_2$: C, 78.77; H, 6.36; N, 7.07. Found: C, 78.62; H, 6.30; N, 6.90.

Diphenyl(trimethylsilylamino)(trimethylsilylimino)-phosphorane, 2c. This compound was synthesized using a literature procedure.[11] Ph_2PH (3.00 mL, 17.2 mmol, d = 1.07) and N_3SiMe_3 (5.00 mL, 35.8 mmol, d = 0.868, 95%) were refluxed overnight in a round-bottom flask with a reflux condenser under a positive pressure of nitrogen. After 12 h the reflux was stopped and the product was distilled through a short path distillation apparatus (0.01 mm, 129 °C) to yield a clear liquid (5.28 g, 85%). Spectral data agreed with literature values. ^{1}H NMR (C_6D_6): δ 7−7.75 (br m, C_6H_5, 10H), 1.88 (br s, N*H*, 1H), 0.34 (s, SiCH_3, 9H), 0.18 (s, SiCH_3, 9H). ^{31}P{^{1}H} NMR (C_6D_6): δ 0.06 (s).

Diethyl(trimethylsilylamino)(trimethylsilylimino)-phosphorane, 2d. Diethylphosphine (2.00 mL, 17.4 mmol, d = 0.7862) and N_3SiMe_3 (5.00 mL, 35.8 mmol, d = 0.868, 95%) were refluxed overnight in a round-bottom flask with a reflux condenser under a positive pressure of nitrogen. After 12 h the product was distilled through a short path distillation apparatus (0.01 mm, 56−60 °C) to yield a clear liquid (3.30 g, 72%). ^{1}H NMR (C_6D_6): δ 1.12 (overlapping dq, CH_2, 4H), 0.84 (overlapping dt, CH_3, J_{HP} = 17.3 Hz, J_{HH} = 7.4 Hz, 6H), 0.73 (br s, N*H*, 1H), 0.29 (s, SiCH_3, 18H). ^{13}C{^{1}H} NMR (C_6D_6): δ 26.6 (d, PCH_2CH$_3$, J_{CP} = 78.2 Hz), 6.5 (d, PCH$_2$*C*H$_3$, J_{CP} = 3.7 Hz), 3.3 (exchange broadened s, $SiMe_3$). ^{31}P{^{1}H} NMR (C_6D_6): δ 20.1. A satisfactory combustion analysis was not obtained for this compound.

Synthesis of [$(CF_3)_2C_6H_3N$][$(CF_3)_2C_6H_3NH$]PPh_2, 2e. Diphenylphosphine (0.365 g, 1.96 mmol) was placed into a Schlenk flask, and toluene (50 mL) was added. The mixture was cooled to 0 °C, and the azide [$(CF_3)_2C_6H_3$]N_3 (1.00 g, 3.92 mmol) in toluene (20 mL) was added dropwise. Little effervescence was initially observed, and only upon warming to room temperature did the reaction became more vigorous. The colorless mixture was stirred overnight at room temperature and then heated to 40 °C for 1 h. The solvent was removed in vacuo to give a white solid (0.826 g, 81%). Recrystallization from cold toluene provided an analytically pure sample as the toluene solvate. Mp: 115−119 °C. ^{1}H NMR (C_6D_6, ambient): δ 7.70−7.60 and 7.00−6.90 (m, 10H, Ph), 7.34 (s, 4H, $((CF_3)_2C_6H_3N))_2$), 7.27 (s, 2H, $((CF_3)_2C_6H_3N))_2$), 5.17 (s, 1H, NH). ^{31}P{^{1}H} NMR (C_6D_6, ambient): δ −2.98. ^{19}F NMR (C_6D_6, ambient): δ −62.94 (s, 12 F). Anal. Calcd for $C_{28}H_{17}F_{12}N_2P\cdot C_7H_8$: C, 57.23; H, 3.70; N, 3.81. Found: C, 57.63; H, 3.39; N, 3.69.

Synthesis of $(C_6F_5N)(C_6F_5NH)PPh_2$, 2f. Diphenylphosphine (1.33 g, 7.14 mmol) was placed into a Schlenk flask, and toluene (50 mL) was added at 0 °C. The azide $C_6F_5N_3$ (3.00 g, 14.3 mmol) in toluene (30 mL) was added dropwise, and the mixture was warmed to room temperature. The reaction was stirred overnight, during which efferevescence ceased. The mixture was heated to 80 °C for 2 h to give a pale yellow solution. The solvent was then removed in vacuo, leaving behind an off-white solid. Recrystallization of the solid from toluene/hexane gave a white solid (2.79 g, 71%). Mp: 125−128 °C. ^{1}H NMR (C_6D_6, ambient): δ 7.90−7.70 and 7.0−6.90 (m, 10H, Ph), 4.22 (s, 1H, NH). ^{31}P{^{1}H} NMR (C_6D_6, ambient): δ 4.78 (s). ^{19}F NMR (C_6D_6, ambient): δ −150.6 (s, br, 4F), −164.8 (s, br, 2F), −165.9 (s, br, 4F). ^{19}F NMR (C_7D_8, −90 °C): δ −144.9 (s, br, 2F), −153.9 (s, br, 1F), −155.2 (s, br, 2F), −162.6 (s, br, 2F), −166.0 (s, br, 1F), −172.0 (s, br, 2F). Anal. Calcd for $C_{24}H_{11}F_{10}N_2P$: C, 52.52; H, 2.02; N, 5.10. Found: C, 52.90; H, 1.68; N, 5.12.

Synthesis of $(C_6F_5N)(C_6F_5NH)PPh_2\cdot$HCl, 1f. Ligand **2f** (0.600 g, 1.09 mmol) was dissolved in toluene (50 mL) in a Schlenk flask. The flask was cooled to 0 °C, and an HCl/ether solution (0.30 mL, 3.8 M) was added. The reaction was warmed to room temperature and the solvent removed in vacuo. The resulting solid was washed with hexane (20 mL) and filtered to give a white solid (0.611 g, 98%). ^{1}H NMR (C_6D_6, ambient): δ 11.90 (s, 2H, NHHCl), 7.91 and 6.77 (m, 10H, Ph). ^{31}P{^{1}H} NMR (C_6D_6, ambient): δ 22.3 (s). ^{19}F NMR (C_6D_6, ambient): δ −142.6 (s, br, 4F), −156.8 (s, br, 2F), −163.8 (t, J = 20.7 Hz, 4F). Anal. Calcd for $C_{24}H_{12}N_2PClF_{10}$: C, 49.29; H, 2.07; N, 4.79. Found: C, 49.30; H, 2.02; N, 4.99.

[$Ph_2P(NCH_2Ph)_2]_2ZrCl_2$, 3a. Compound **1a** (5.083 g, 11.74 mmol) was slowly added to a solution of $Zr(NMe_2)_4$ (1.57 g, 5.87 mmol) in toluene (200 mL) and allowed to stir for several hours. Partial vacuum was applied periodically throughout the reaction to ensure that there was always a negative pressure inside the flask. After 12 h the toluene was removed in vacuo, and spectral data were obtained. The product was purified by recrystallization from CH_2Cl_2/hexanes. In this fashion 4.95 g of a white solid was obtained (88%). ^{1}H NMR (C_6D_6): δ 7.60−7.55, 7.32−7.27, and 7.15−6.87 (br m, 40H, C_6H_5), 4.62 (d, 8H, CH_2Ph, $^3J_{HP}$ = 26 Hz). ^{13}C NMR ($CDCl_3$): δ 141.2, 133.2−132.0, and 128.8−126.4 (C_6H_5), 51.7 (*C*H$_2$Ph). ^{31}P NMR (CH_2Cl_2): δ 45.8. Anal. Calcd for $C_{52}H_{48}PN_4ZrCl_2$: C, 65.53; H, 5.08; N, 5.88. Found: C, 65.72; H, 5.29; N, 5.81. Single crystals were

obtained by dissolving the solid in a minimal amount of hot toluene and allowing it to stand overnight.

[$Ph_2P(NCH_2Ph)_2]_2TiCl_2$, 3b. Ligand salt **1a** (3.55 g, 8.21 mmol) was dissolved with 150 mL of dry CH_2Cl_2 in a 500 mL Schlenk flask. A 50 mL toluene solution of $Ti(NMe_2)_4$ (0.918 g, 4.09 mmol) was added to the flask rapidly by syringe. The reaction mixture was stirred for 30 min, and volatiles were removed under vacuum. Bright yellow crystals of complex **3a** were obtained by crystallization from CH_2Cl_2 and hexane. Yield: 82%. ^{1}H NMR ($CDCl_3$): δ 7.5−6.9 (40H, aromatic protons), 4.65 (d, 8H, NCH_2Ph, $^3J_{PH}$ = 25.5 Hz). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 141.0, 133.7, 133.5, 132.2, 132.2, 129.2, 128.0, 127.8, 127.5, 126.6 (aromatic carbons), 55.3 (NCH_2Ph). ^{31}P{^{1}H} NMR (CH_2Cl_2): δ 47.3. Anal. Calcd for $C_{52}H_{48}N_4P_2Cl_2Ti$: C, 68.66; H, 5.32; N, 6.15. Found: C, 69.05; H, 5.14; N, 6.00.

[$Ph_2P(N$-p-tolyl$)_2]_2ZrCl_2$, 3c. Compound **1b** (7.000 g, 16.17 mmol) was slowly added to a solution of $Zr(NMe_2)_4$ (2.16 g, 8.08 mmol) in toluene (200 mL) and allowed to stir for several hours at room temperature. The reaction was worked up as described above for the preparation of **3a** to produce a white solid (6.54 g, 85%). ^{1}H NMR ($CDCl_3$): δ 7.54−7.45 and 7.28−7.21 (br m, 10H, C_6H_5), 6.89 (d, 4H, m-$C_6H_4CH_3$, $^3J_{HH}$ = 8.2 Hz), 6.72 (dd, 4H, o-$C_6H_4CH_3$, $^3J_{HH}$ = 8.2 Hz, $^3J_{PH}$ = 1.9 Hz), 2.28 (s, 6H, $C_6H_4CH_3$). ^{13}C NMR ($CDCl_3$): δ 143.1, 133.6−132.2 and 129.2−125.6, and 116.4 (C_6H_5 and $C_6H_4CH_3$), 20.8 ($C_6H_5CH_3$). ^{31}P NMR (CH_2Cl_2): δ 34.8. Anal. Calcd for $C_{52}H_{48}P_2N_4ZrCl_2$: C, 65.53; H, 5.08; N, 5.88. Found: C, 65.36; H, 5.20; N, 5.74.

[$Ph_2P(N$-p-tolyl$)_2]_2TiCl_2$, 3d. Phosphonium salt **1b** (3.55 g, 8.21 mmol) was dissolved with 150 mL of dry CH_2Cl_2 in a 500 mL Schlenk flask. A 50 mL toluene solution of $Ti(NMe_2)_4$ (0.918 g, 4.09 mmol) was added to the flask rapidly by syringe. The reaction mixture was stirred for 30 min, and volatiles were removed under vacuum. The remaining solid was dissolved with 50 mL of CH_2Cl_2, and 100 mL of hexane was carefully added on the top of the CH_2CL_2 layer. The mixture was left undisturbed overnight, and purple crystals formed. These crystals contained 1 equiv of CH_2Cl_2 solvent (as shown by NMR and elemental analysis). The solvent-free complex **6** was obtained by dissolving the crystals in toluene and then removing the volatiles. Yield: 3.16 g (3.48 mmol, 85%). ^{1}H NMR ($CDCl_3$): δ 7.4−6.8 (36H, aromatic protons), 2.27 (s, 12H, NPhCH_3). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 146.4, 134.0, 133.8, 132.8, 132.5, 128.8, 128.1, 127.9, 125.2 (aromatic carbons), 20.9 (NPhCH_3). ^{31}P{^{1}H} NMR (CH_2Cl_2): δ 36.5. Anal. Calcd for $C_{53}H_{50}N_4P_2Cl_4Ti$: C, 64.07; H, 4.97; N, 5.64. Found: C, 64.35; H, 4.94; N, 5.72.

Synthesis of [$(C_6F_5N)_2PPh_2]_2ZrCl_2$, 3e. Method A. Ligand salt **1f** (1.00 g, 1.71 mmol) was added in small portions to a solution of $Zr(NMe_2)_4$ (0.229 g, 0.856 mmol) in toluene (60 mL) at −30 °C. The reaction was warmed to room temperature and stirred overnight to give a clear solution. The solvent was removed in vacuo to give a white solid. The solid was stirred with hexane (50 mL) and filtered off. Recrystallization from toluene (20 mL) gave a white powder (0.887 g, 79%). ^{1}H NMR (C_6D_6, ambient): δ 7.72−7.62 and 7.00 (m, 20H, Ph). ^{31}P{^{1}H} NMR (C_6D_6, ambient): δ 47.4 (s). ^{19}F NMR (C_6D_6, ambient): δ −142.6 (d, 8F, J = 20.7 Hz), −161.2 (t, 4F, J = 22.6 Hz), −163.8 (t, 8F, J = 21.7 Hz). Anal. Calcd for $C_{48}H_{20}N_4P_2Cl_2F_{20}Zr$: C, 45.87; H, 1.60; N, 4.45. Found: C, 45.50; H, 1.54; N, 4.56.

Method B. $Zr(NMe_2)_4$ (0.244 g, 0.912 mmol) was placed into a Schlenk flask, and toluene (60 mL) was added at −30 °C. Ligand **2f** (1.00 g, 1.82 mmol) in toluene (20 mL) was added dropwise to the solution. The mixture was warmed to room temperature and stirred overnight to give a pale yellow solution. The solvent was removed in vacuo to give a white solid, which was washed with hexane (50 mL) and filtered off to provide bis(dimethylamido) complex of sufficient purity for further use (1.04 g, 89%). ^{1}H NMR (C_6D_6, ambient): δ 7.50−7.40 and 7.00 (m, 20H, Ph), 2.96 (s, 12H, NMe_2). ^{31}P{^{1}H} NMR (C_6D_6, ambient): δ 41.0 (s). ^{19}F NMR (C_6D_6, ambient): δ −143.8 (d, 8F, J = 20.7 Hz), −164.4 (t, 4F, J = 19.8 Hz), −164.9 (t, 8F, J = 22.6 Hz)

This amido complex (1.00 g, 0.768 mmol) was dissolved in toluene (60 mL) in a Schlenk flask and cooled to 0 °C. Chlorotrimethylsilane (0.21 mL, 1.65 mmol) was added, and the reaction was warmed to room temperature and then heated at 50 °C overnight. The solvent was removed in vacuo, and the white residue was dissolved in toluene (50 mL) and filtered via a Celite pad to give a pale yellow filtrate. The solvent was removed in vacuo to ca. 20 mL and the flask placed into a −30 °C freezer to give a white solid (0.817 g, 85%).

Synthesis of [Me_2NH_2][$Ph_2P(NTMS)_2$]$ZrCl_4$], 4. A solution of ligand **2c** (2.294 g, 6.4 mmol) in a minimal volume of toluene was added to a solution of $Zr(NMe_2)_4$ (1.702 g, 6.4 mmol) in toluene at 25 °C with stirring. The solution turned yellow immediately, and the flask was evacuated to remove dimethylamine. After subsequent stirring for 48 h at 25 °C, the solution was concentrated in vacuo to provide crude tris(dimethylamido) complex, sufficiently pure for further use (3.523 g, 95%). ^{1}H NMR (C_6D_6, 25 °C): δ 7.9−7.8 (br m, 4H, Ph) 7.12−7.08 (m, 6 H, Ar), 3.19 (s, 18 H, NMe_2), 0.04 (s, 18H, $SiMe_3$).

A solution of the above complex (0.300 g, 0.51 mmol) in CH_2Cl_2 was stirred with an excess of $Me_2NH{\cdot}HCl$ (0.166 g, 2.04 mmol) at room temperature for a period of 12 h, during which time all of the hydrochloride salt dissolved. The mixture was evaporated to dryness in vacuo. This afforded a mixture of the title compound (major) and what appears to be $[Ph_2P(NTMS)_2]ZrCl_3{\cdot}(Me_2NH)_2$. Crystallization from a mixture of CH_2Cl_2 and toluene provided single crystals of the title compound, the structure of which was confirmed by X-ray crystallography. Anal. Calcd for $C_{20}H_{36}N_3Cl_4Si_2PZr$: C, 37.61; H, 5.68; N, 6.58. Found: C, 37.25; H, 5.97; N, 6.23.

[$Ph_2P(NCH_2Ph)_2]_2ZrMe_2$, 5a. Complex **3a** (1.50 g, 1.57 mmol) was placed in a Schlenk flask with 100 mL of toluene. MeLi (1.908 mL, 1.65 M in ether, 3.14 mmol) was added via syringe to the solution at room temperature over about 5 min. The mixture was allowed to stir for 1 h, and then the solvent was removed in vacuo. The solids were redissolved in about 10 mL of CH_2Cl_2 and then filtered through Celite. The flask and Celite were washed with two additional portions of CH_2Cl_2. Removal of solvent resulted in a white, crystalline powder (1.10 g, 77%). ^{1}H NMR (C_6D_6): δ 7.57−7.50 and 7.27−6.93 (br m, 40H, C_6H_5), 4.48 (d, 8H, C$H_2C_6H_5$, $^3J_{PH}$ = 26 Hz), 1.15 (s, 6H, CH_3). ^{13}C NMR ($CDCl_3$): δ 142.8 and 132.6−125.8 (C_6H_5), 49.9 (CH_2Ph), 40.0 (t, ZrCH_3, $^3J_{CP}$ = 3.4 Hz). ^{31}P NMR (CH_2Cl_2): δ 48.0. Anal. Calcd for $C_{54}H_{54}P_2N_4Zr$: C, 71.10; H, 5.97; N, 6.14. Found: C, 71.05; H, 5.87; N, 5.90.

[$Ph_2P(NCH_2Ph)_2]_2TiMe_2$, 5b. Complex **3b** (1.22 g, 1.34 mmol) was dissolved with 100 mL of toluene in a 250 mL flask, and the resulting solution was cooled to −30 °C. A solution of MeLi in ether (1.63 mL, 1.65 M, 2.68 mmol) was added rapidly. The reaction mixture was allowed to warm to room temperature and stirred for 30 min. The remaining material was extracted with toluene. The volume of extract was reduced to 15 mL; layering this solution with 30 mL of hexane provided complex **5b** (0.95 g, 1.10 mmol) as orange-red crystals. Yield: 82%. ^{1}H NMR ($CDCl_3$): δ 7.5−6.9 (40H, aromatic protons), 4.24 (d, 8H, NCH_2Ph, $^3J_{PH}$ = 27.1 Hz), 1.30 (s, 6H, TiCH_3). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 142.9, 133.2, 133.0, 131.7, 131.2, 129.9, 129.3, 128.4, 128.0, 127.9, 127.6, 125.8 (aromatic carbons), 62.7 (TiCH_3), 51.7 (NCH_2Ph). ^{31}P{^{1}H} NMR (CH_2Cl_2): δ 49.9. Anal. Calcd for $C_{54}H_{54}N_4P_2Ti$: C, 74.64; H, 6.26; N, 6.44. Found: C, 74.24; H, 5.96; N, 6.55.

[$Ph_2P(N$-p-tolyl$)_2]_2ZrMe_2$, 5c. Complex **3c** (1.0 g, 1.05 mmol) was placed in a Schlenk flask with toluene (50 mL), and MeLi (1.61 mL, 2.10 mmol) was syringed in and the solution was allowed to stir for 1 h. After this time the toluene was removed in vacuo and the solid was redissolved in CH_2Cl_2 and filtered. The solvent was removed in vacuo to give a white,

crystalline powder. ^{1}H NMR (THF-d_8): δ 7.61−7.08 (br m, 20H, C_6H_5), 6.76 and 6.61 (d, 16H, $C_6H_4CH_3$, $^3J_{HH}$ = 8.0 Hz), 2.19 (s, 12H, $C_6H_4CH_3$), 0.30 (s, 6H, Zr−CH_3). ^{13}C NMR ($CDCl_3$): δ 143.9 and 133.2−125.2 (C_6H_5 and $C_6H_4CH_3$), 43.6 (t, ZrCH_3, $^3J_{CP}$ = 3.2 Hz), 20.7 ($C_6H_4CH_3$). ^{31}P NMR (CH_2Cl_2): δ 35.0. Anal. Calcd for $C_{54}H_{54}P_2N_4Zr$: C, 71.10; H, 5.97; N, 6.14. Found: C, 71.55; H, 5.85; N, 5.92.

[Ph_2P(*N*-*p*-tolyl)$_2$]$_2$TiMe$_2$, 5d. Complex **3d** (1.40 g, 1.54 mmol) was dissolved with 150 mL of toluene in a 500 mL Schlenk flask, and the resulting solution was cooled to 0 °C. A solution of MeMgBr in ether (1.2 mL, 2.6 M, 3.1 mmol) was added to the flask rapidly by syringe, which resulted in an immediate color change from deep red to yellow. The reaction mixture was allowed to stir for 30 min at 0 °C, and volatiles were then removed under vacuum. The remaining material was extracted with toluene. The volume of extract was reduced to 15 mL; layering this solution with 30 mL of hexane provided 1.0 g of crystals. Yield: 75%. ^{1}H NMR ($CDCl_3$): δ 7.5−6.6 (36H, aromatic protons), 2.25 (s, 6H, NPhCH_{3a}), 2.24 (s, 6H, NPhCH_{3b}), 1.23 (TiCH_3). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 145.5, 133.6, 133.5, 133.4, 133.3, 131.7, 131.6, 131.4, 130.9, 130.1, 128.8, 128.0, 127.8, 125.7, 125.6 (aromatic carbons), 69.9 (TiCH_3), 20.8 (N-Ph-CH_3). ^{31}P{^{1}H} NMR (CH_2Cl_2): δ 38.0. Anal. Calcd for $C_{54}H_{54}N_4P_2Ti$: C, 74.64; H, 6.26; N, 6.44. Found: C, 74.40; H, 5.89; N, 5.93.

[Ph_2P(*N*-*p*-tolyl)$_2$]$_2$Zr(CH_2Ph)$_2$, 5e. Complex **3c** (2.00 g, 2.10 mmol) was placed in a Schlenk flask along with toluene (100 mL). Powdered KCH_2Ph (547 mg, 4.20 mmol) was slowly added with stirring. The mixture was allowed to stir for 1 week before the red color of the KCH_2Ph disappeared to give a yellow solution. The solvent was removed in vacuo, and the resulting solid was redissolved in a small amount of toluene and filtered through Celite. The solid and Celite are washed with two more portions of toluene (20 mL). The filtrate volume was reduced, and yellow, single crystals were obtained by layering the solution with hexanes (1.243 g, 56%). ^{1}H NMR ($CDCl_3$): 7.41−6.46 (br m, 46H, C_6H_5 and $C_6H_4CH_3$), 2.41 (s, 4H, CH_2Ph), 2.23 ($C_6H_5CH_3$). ^{31}P NMR (CH_2Cl_2): δ 36.2.

Cp[$Ph_2P(NCH_2Ph)_2$]ZrCl$_2$, 6a. Method A. A solution of $CpZr(NMe_2)_3$ (1.00 g, 3.47 mmol) in toluene (50 mL) was prepared in a Schlenk flask. Ligand **2a** (1.37 g, 3.47 mmol) was slowly added to the solution at room temperature. Vacuum was applied to remove the dimethylamine that was liberated. The solution was allowed to stir overnight. The next day, Me_2NH_2Cl (565 mg, 6.93 mmol) was added. The solid slowly dissolved in about 6 h, and vacuum was applied to remove the Me_2NH. After 24 h the solution was reduced almost to dryness and then layered with hexane, producing a white solid. This was washed twice with pentane and dried under vacuum (yield 1.764 g, 82%).

Method B. A solution of $CpZr(NMe_2)_3$ (1.50 g, 5.20 mmol) and salt **1a** (2.25 g, 5.20 mmol) in toluene (50 mL) was prepared. This was stirred overnight. The next day, Me_2NH_2Cl (424 mg, 5.20 mmol) was added and the solution was allowed to stir overnight until the entire solid had dissolved. Partial vacuum was applied to remove Me_2NH as it was produced. A solid was obtained by reducing the volume of the solution almost to dryness and then adding about 100 mL of pentane. The white solid was collected, washed with pentane, and dried in vacuo (2.88 g, 90%). ^{1}H NMR ($CDCl_3$): δ 7.67−6.92 (br m, 20H, C_6H_5), 6.12 (s, 5H, C_5H_5), 4.22 (d, 4H, CH_2Ph, $^3J_{HP}$ = 21 Hz). ^{13}C NMR ($CDCl_3$): δ 140.4, 132.9−132.5, and 129.2−127.0 (C_6H_5), 115.5 (C_5H_5), 51.7 (CH_2Ph). ^{31}P NMR (CH_2Cl_2): δ 36.8. Anal. Calcd for $C_{31}H_{29}PN_2ZrCl_2$: C, 59.80; H, 4.69; N, 4.50. Found: C, 59.82; H, 4.95; N, 4.25.

Cp[Ph_2P(*N*-*p*-tolyl)$_2$]ZrCl$_2$, 6b. $CpZr(NMe_2)_3$ (2.00 g, 6.94 mmol) and compound **1b** (3.00 g, 6.94 mmol) were placed in a Schlenk flask along with toluene (100 mL). The solution was allowed to stir overnight. After 12 h, Me_2NH_2Cl (560 mg, 6.94 mmol) was added and the solution was stirred overnight so that the entire solid had dissolved. The volume of the solution was reduced until a solid began to precipitate. The solution was reduced some more (5 mL), and hexanes (100 mL) were added to precipitate all of the material. The mixture was filtered, and the solid was washed with 2 × 20 mL of hexanes. The white solid was dried under vacuum (3.27 g, 77%). ^{1}H NMR ($CDCl_3$): δ 7.76−7.49 (br m, 10H, C_6H_5), 6.90 (d, 4H, *m*-$C_6H_4CH_3$, $^3J_{HH}$ = 8.2 Hz), 6.68 (s, 5H, C_5H_5), 6.61 (dd, 4H, *o*-$C_6H_4CH_3$, $^3J_{HH}$ = 8.3 Hz, $^4J_{HP}$ = 1.7 Hz), 2.22 (s, 6H, $C_6H_5CH_3$). ^{13}C NMR ($CDCl_3$): δ 142.9 and 133.2−124.9 (C_6H_5 and $C_6H_4CH_3$), 116.4 (C_5H_5), 20.7 ($C_6H_4CH_3$). ^{31}P NMR (CH_2Cl_2): δ 31.9. Anal. Calcd for $C_{31}H_{29}PN_2ZrCl_2$: C, 59.80; H, 4.69; N, 4.50. Found: C, 59.40; H, 4.97; N, 4.26.

Synthesis of Cp*Zr[(*p*-$CH_3(C_6H_4)$N)$_2$$PPh_2$]Cl$_2$, 6c. A solution of $Cp^*Zr(NMe_2)_3$ (1.00 g, 2.79 mmol) was placed into a Schlenk flask, and hexane (60 mL) was added. The solution was cooled to −30 °C, and ligand **2b** (1.11 g, 2.79 mmol) in toluene (40 mL) was added dropwise to the flask. The reaction was allowed to warm to room temperature and stirred overnight to give a pale yellow solution. Next, the solvent was removed in vacuo to give a yellow residue that was extracted with two portions of hexane (2 × 50 mL) and passed through Celite to give a pale yellow filtrate. The solvent was removed in vacuo to ca. 20 mL and placed in a −30 °C freezer to give bis(amido) complex as a pale yellow solid, sufficiently pure for the next step (1.33 g, 67%). ^{1}H NMR (C_6D_6, ambient): δ 7.92−7.80 and 6.99 (m, 10H, Ph), 6.90 and 6.86 (d, 8H, J = 8.2 Hz, $C_6H_4CH_3$), 3.10 (s, 12H, NMe_2), 2.17 (s, 15H, Cp*), 2.10 (s, 6H, $C_6H_4CH_3$). ^{31}P{^{1}H} NMR (C_6D_6, ambient): δ 28.0 (s).

This bis(amido) complex (1.10 g, 1.55 mmol) was placed into a Schlenk flask, and toluene (60 mL) was added flask at 0 °C. Me_3SiCl (0.41 mL, 3.23 mol) was added to the flask and the mixture warmed to room temperature. The flask was heated to 50 °C and stirred overnight to give a cloudy yellow solution. The solvent was removed in vacuo, and the yellow residue was dissolved in toluene (100 mL) and filtered via a Celite pad. The solvent was then removed in vacuo to ca. 20 mL and an equal volume of hexane added to give an off-white powder (0.852 g, 79%). ^{1}H NMR (C_6D_6, ambient): δ 7.76−7.67 and 6.94 (m, 10H, Ph), 6.96 and 6.82 (d, 4H, J = 8.1 Hz, $C_6H_4CH_3$), 2.17 (s, 15H, Cp*), 2.01 (s, 6H, $C_6H_4CH_3$). ^{31}P{^{1}H} NMR (C_6D_6, ambient): δ 31.5 (s). Anal. Calcd for $C_{36}H_{39}N_2PCl_2Zr$: C, 62.41; H, 5.67; N, 4.04. Found: C, 62.44; H, 5.67; N, 4.18.

Cp[$Ph_2P(NSiMe_3)_2$]ZrCl$_2$, 6d. A solution of ligand **2c** (1.400 g, 3.88 mmol) in toluene (100 mL) was slowly added to a solution of $CpZr(NMe_2)_3$ (1.120 g, 3.88 mmol) in toluene to form a yellow solution. This solution was stirred for 10 min, and then NMe_2H_2Cl (0.633 g, 7.77 mmol) was added and the mixture was allowed to stir overnight until all of the solid had dissolved. The solution became colorless overnight. The solvent was removed in vacuo, and the resulting solid was dissolved in about 5 mL of CH_2Cl_2, to which 20 mL of hexanes was added. The volume was reduced to about 5 mL, and another 20 mL of hexanes was added. This process was repeated several times until a large amount of white solid precipitated. This gave 1.80 g (79%) of a pure (by ^{1}H NMR spectroscopy) white solid. ^{1}H NMR (C_6D_6): δ 7.85−7.77 and 7.11−7.01 (br m, 10 H, C_6H_5), 6.57 (s, 5H, C_5H_5), 0.003 (s, 18H, SiCH_3). ^{13}C NMR ($CDCl_3$): δ 132.6−128.4 (aromatic C), 116.3 (C_5H_5), 2.80 (SiCH_3). ^{31}P NMR (CH_2Cl_2): δ 22.2. Anal. Calcd for $C_{23}H_{33}PN_2Si_2ZrCl_2$: C, 47.08; H, 5.67; N, 4.77. Found: C, 48.15; H, 5.70; N, 4.25.

Cp[$Et_2P(NSiMe_3)_2$]ZrCl$_2$, 6e. A solution was made of ligand **2d** (0.700 g, 2.65 mmol) and $CpZr(NMe_2)_3$ (0.764 g, 2.65 mmol) in toluene (100 mL). The yellow solution was allowed to stir for about 10 min, and then NMe_2H_2Cl (0.432 g, 7.56 mmol) was added. The solution rapidly turned colorless and was allowed to stir overnight. In the same manner as described for the preparation of **6d**, the solvent was removed under vacuum and the resulting solid was recrystallized from CH_2Cl_2/hexanes. This gave an initial batch of white, single crystals (0.580 g), and the filtrate was further concentrated to yield

another 0.515 g of a pure white powder (total = 1.095 g, 85%). ^{1}H NMR (C_6D_6): δ 6.40 (s, 5H, C_5H_5), 1.10 (dq, 4H, CH_2CH_3), 0.85 (dt, 6H, CH_2CH_3). ^{13}C NMR ($CDCl_3$): δ 116.2 (C_5H_5), 25.2 (d, CH_2CH_3, $^1J_{CP}$ = 65 Hz), 5.07 (d, CH_2CH_3, $^2J_{CP}$ = 6.0 Hz), 2.70 (d, $SiCH_3$, $^3J_{CP}$ = 2.9 Hz). ^{31}P NMR (CH_2Cl_2): δ 44.2. Anal. Calcd for $C_{15}H_{33}PN_2Si_2ZrCl_2$: C, 36.72; H, 6.78; N, 5.71. Found: C, 36.50; H, 6.56; N, 5.54.

Synthesis of CpZr{[(CF$_3$)$_2$C$_6$H$_3$N)}$_2$PPh$_2$]Cl$_2$, 6f. $CpZr(NMe_2)_3$ (0.451 g, 1.56 mmol) was added to a Schlenk flask containing toluene (50 mL) at −30 °C. Ligand **2e** (1.00 g, 1.56 mmol) in toluene (50 mL) was added dropwise into the reaction flask, and the mixture was warmed to room temperature. The mixture was stirred overnight at room temperature to give a yellow solution. The solvent was evaporated in vacuo to ca. 20 mL and placed in a −30 °C freezer to give yellow crystals, sufficiently pure for further use (1.05 g, 80%). ^{1}H NMR (C_6D_6, ambient): δ 7.70−7.58 and 6.94 (m, 10H, Ph), 7.33 (s, 2H, ((CF_3)$_2$$C_6H_3N$)), 7.15 (s, 4H, (($CF_3$)$_2$$C_6H_3N$), 6.25 (s, 5H, Cp), 2.84 (s, 12H, NMe_2). ^{31}P{^{1}H} NMR (C_6D_6, ambient): δ 33.2 (s). ^{19}F NMR (C_6D_6, ambient): δ −62.9 (s, 12F, CF_3).

The amido complex (0.702 g, 0.794 mmol) was placed into a Schlenk flask, and toluene (50 mL) was added at −30 °C. Me_3SiCl (0.21 mL, 1.65 mmol) was added and the yellow mixture stirred to room temperature. After stirring overnight, the mixture was heated to 60 °C for 2 h, resulting in a colorless solution. The solvent was removed in vacuo to ca. 20 mL and placed in a −30 °C freezer to give a white solid (0.522 g, 66%). ^{1}H NMR (C_6D_6, ambient): δ 7.38 (s, 2H, ((CF_3)$_2$$C_6H_3N$)), 7.32 (s, 4H, (($CF_3$)$_2$$C_6H_3N$), 6.97−6.91 and 6.85−6.82 (m, 10H, Ph), 6.29 (s, 5H, Cp). ^{31}P{^{1}H} NMR (C_6D_6, ambient): δ 37.0 (s). ^{19}F NMR (C_6D_6, ambient): δ −62.9 (s, 12F, CF_3). A satisfactory combustion analysis was not obtained for this compound.

Synthesis of Cp*Zr{[(CF$_3$)$_2$C$_6$H$_3$N)]$_2$PPh$_2$}Cl$_2$, 6g. $Cp^*Zr(NMe_2)_3$ (0.920 g, 2.56 mmol) was placed into a Schlenk flask, and toluene (50 mL) was added at −30 °C. Then ligand **2e** (1.64 g, 2.56 mmol) in toluene (20 mL) was added dropwise, and the reaction mixture was allowed to warm to room temperature. The mixture was stirred overnight to give a pale yellow solution. The reaction was then warmed to 30 °C for 6 h and the solvent then removed in vacuo, leaving behind a yellow solid. The solid was dissolved in two portions of hexane (2 × 50 mL) and filtered via Celite to give a yellow solution. Removal of the solvent in vacuo to ca. 20 mL and placement into a −30 °C freezer gave a yellow solid, sufficiently pure for further use (2.10 g, 86%). ^{1}H NMR (C_6D_6, ambient): δ 7.74−7.65 and 7.00−6.80 (m, 10H, Ph), 7.45 (s, 4H,((CF_3)$_2$$C_6H_3N$)), 7.35 (s, 2H, (($CF_3$)$_2$$C_6H_3N$)), 2.88 (s, 12H, NMe_2), 1.98 (s, 15H, Cp*). ^{31}P{^{1}H} NMR (C_6D_6, ambient): δ 32.7 (s). ^{19}F NMR (C_6D_6, ambient): δ −62.6 (s, 12F, CF_3)

The amido complex (0.859 g, 0.900 mmol) was placed into a Schlenk flask, and toluene (50 mL) was added at −30 °C. Me_3SiCl (0.24 mL, 1.89 mmol) was added to the flask and the mixture warmed to room temperature to give a pale yellow solution. The reaction was stirred overnight and then heated to 60 °C for 1 h. The solvent was removed in vacuo to ca. 20 mL and placed in a −30 °C freezer to give a pale yellow solid (0.533 g, 63%). ^{1}H NMR (C_6D_6, ambient): δ 7.47 (s, 4H, ((CF_3)$_2$$C_6H_3N$)), 7.36 (s, 2H, (($CF_3$)$_2$$C_6H_3N$)), 6.95−6.90 and 6.82 (m, 10H, Ph), 2.02 (s, 15H, Cp*). ^{31}P{^{1}H} NMR (C_6D_6, ambient): δ 35.6 (s). ^{19}F NMR (C_6D_6, ambient): δ −62.9 (s, 12F, CF_3). Anal. Calcd for $C_{38}H_{31}N_2PCl_2F_{12}Zr$: C, 48.72; H, 3.33; N, 2.99. Found: C, 48.57; H, 3.32; N, 2.99.

Synthesis of CpZr[(C$_6$F$_5$N)(C$_6$F$_4$N)PPh$_2$]Cl$_2$, 6h. $CpZr(NMe_2)_3$ (0.263 g, 0.911 mmol) in toluene (50 mL) was prepared in a Schlenk flask and cooled to −78 °C. Ligand **2f** (0.500 g, 0.911 mmol) in toluene (20 mL) was added dropwise to the flask. After complete addition, the mixture was stirred at −78 °C for 1.5 h. Next, a HCl/ether solution (0.50 mL, 4 M) in toluene (10 mL) was added dropwise to the flask. The reaction was stirred at −78 °C for 0.5 h and then warmed to room temperature, at which time the solvent was removed in vacuo. The resulting white solid was stirred with hexane (30 mL) and filtered off (0.406 g, 57%). ^{1}H NMR (C_6D_6, ambient): δ 7.60−7.45 and 7.05−6.85 (m, 10H, Ph), 6.47 (s, 5H, Cp). ^{31}P{^{1}H} NMR (C6D6, ambient): δ 45.0 (s). ^{19}F NMR (C_6D_6, ambient): δ −142.6 (d, 4F, J = 22.6 Hz), −159.4 (t, 2F, J = 21.7 Hz), −163.3 (t, 4F, J = 22.6 Hz). Anal. Calcd for $C_{29}H_{15}N_2PCl_2F_{10}Zr$: C, 44.97; H, 1.95; N, 3.61. Found: C, 44.64; H, 1.80; N, 3.85.

Synthesis of CpZr{[2-(NMe$_2$)C$_6$F$_4$N]$_2$PPh$_2$}F$_2$, 7a, and CpZr{(C$_6$F$_5$N)[2,6-(NMe$_2$)$_2$C$_6$F$_4$N]}PPh$_2$]F$_2$, 7b. $CpZr(NMe_2)_3$ (1.00 g, 3.47 mmol) in toluene (50 mL) was prepared in a Schlenk flask and cooled to −30 °C. Ligand **2f** (1.90 g, 3.47 mmol) in toluene (30 mL) was added dropwise, and the mixture was warmed to room temperature to give a pale yellow solution. The mixture was further stirred for 2 days and the solvent then removed in vacuo. The resulting white solid was washed with hexane (20 mL) and filtered off to give 1.79 g of **7a** and **7b**. The solid mixture was dissolved in toluene (50 mL) and filtered through Celite. The filtrate was removed in vacuo to ca. 20 mL and placed in the freezer (−30 °C) to give 1.07 g of complex **7a** as a white crystalline solid, while leaving the mother liquor at −30 °C gave 0.408 g of complex **7b** as a white solid. Complex **7a**: ^{1}H NMR (C_6D_6, ambient): δ 8.15 and 7.48 and 6.98 (s, br, 10H, Ph), 6.23 (s, 5H, Cp), 3.15 and 3.04 and 2.27 (s, br, 12H, NMe_2). ^{31}P{^{1}H} NMR (C_6D_6, ambient): δ 36.7 (s) 31.4 (s). ^{19}F NMR (C_6D_6, ambient): δ 81.6 (d, J = 36.6 Hz), 63.2 (d, J = 97.7 Hz), 46.7 (d, J = 36.6 Hz), 42.9 (d, J = 97.7 Hz), −142.0 (s, br, 1F), −145.9 (d, 2F, J = 24.4 Hz), −145.9 (s, br, 1F), −150.6 (s, br, 1F), −158.8 (s, br, 1F), −159.8 (t, 1F, J = 24.4 Hz), −161.9 (s, br, 1F), −164.0 (s, br, 1F), −171.1 (t, 1F, J = 24.4 Hz), −171.4 (s, br, 1F). ^{19}F NMR (C_7D_8, −60 °C): δ 80.5 (d, 1F, J = 36.6 Hz), 42.2 (d, 1F, J = 36.6 Hz), −146.1 (d, 2F, J = 24.4 Hz), −147.7 (d, 2F, J = 24.4 Hz), −159.4 (t, 2F, J = 24.4 Hz), −170.7 (br, 2F). Anal. Calcd for $C_{33}H_{27}N_4PF_{10}Zr\cdot C_7H_8$: C, 54.35; H, 3.99; N, 6.34. Found: C, 54.76; H, 3.87; N, 6.25. Complex **7b**: ^{1}H NMR (C_6D_6, ambient): δ 7.93 and 7.02 (s, br, 10H, Ph), 6.15 (s, 5H, Cp), 3.12 (s, 6H, NMe_2), 1.40 (s, 6H, NMe_2). ^{31}P{^{1}H} NMR (C_6D_6, ambient): δ 36.3 (s). ^{19}F NMR (C_6D_6, ambient): δ 30.9 (s, 2F), −141.2 (d, 1F, J = 22.6 Hz), −144.1 (d, 1F, J = 22.6 Hz), −144.6 (d, 2F, J = 22.6 Hz), −160.5 (t, 1F, J = 23.5 Hz), −164.1 (t, 2F, J = 22.6 Hz), −171.8 (t, 1F, J = 20.7 Hz). Anal. Calcd for $C_{33}H_{27}N_4PF_{10}Zr$: C, 50.06; H, 3.44; N, 7.08. Found: C, 49.70; H, 3.22; N, 6.79.

Cp[Ph$_2$P(NCH$_2$Ph)$_2$]ZrMe$_2$, 8a. Complex **6a** (1.00 g, 1.61 mmol) was placed in a Schlenk flask, and THF (25 mL) was added. The mixture was cooled to 0 °C, and MeMgBr (1.24 mL in THF, 3.22 mmol) was added rapidly via syringe. The solution was allowed to warm to room temperature and stirred for 10 min. Then the solution volume was reduced to about 2 mL, 25 mL of toluene was added, and the volume was reduced again. This process was repeated about 3 or 4 times until no more THF was seen in the ^{1}H NMR spectrum of the crude material. The residual solid was dissolved in a small amount of CH_2Cl_2, the volume was reduced to about 1−2 mL, and hexanes (20 mL) were added. This process was repeated 2 or 3 times to produce a white precipitate, which ^{1}H NMR spectra showed to be pure product (0.510 g, 55%). ^{1}H NMR (C_6D_6): δ 7.51−7.46 and 7.15−6.92 (br m, 20H, C_6H_5), 6.11 (s, 5H, C_5H_5), 4.24 (d, 4H, CH_2Ph, $^3J_{HP}$ = 23.5 Hz), 0.53 (s, 6H, $ZrCH_3$). ^{13}C NMR (C_6D_6): δ 142.6, 132.6−126.5 (C_6H_5), 111.8 (C_5H_5), 50.3 (CH_2Ph), 39.4 ($ZrCH_3$). ^{31}P NMR (CH_2Cl_2): δ 45.2. Anal. Calcd for $C_{33}H_{35}N_2PZr$: C, 68.12; H, 6.06; N, 4.81. Found: C, 68.29; H, 6.06; N, 4.69.

Cp[Ph$_2$P(NCH$_2$Ph)$_2$]TiMe$_2$, 8b. $CpTiCl_3$ (1.00 g, 4.56 mmol) was dissolved with 100 mL of toluene in a 500 mL Schlenk flask and was cooled to −30 °C. A solution of methyllithium in 8.5 mL of ether (1.6 M, 13.6 mmol) was added to the flask rapidly by syringe. The reaction mixture was stirred at −30 °C for 5 min, and then 25 mL of a toluene solution of ligand **2a** (1.80 g, 4.56 mmol) was added rapidly. The mixture was allowed to warm to room temperature and

stirred for 30 min, and then volatiles were removed under vacuum. The remaining material was extracted with toluene. Removal of toluene from the extract gave an orange-red powder that was further purified by recrystallization from a toluene/hexane mixture to give orange-red crystals. Yield: 50%. ^{1}H NMR ($CDCl_3$): δ 7.7−6.7 (20H, aromatic protons), 5.96 (s, 5H, Cp-protons), 4.04 (d, 4H, NCH_2Ph, $^3J_{PH}$ = 22.5 Hz), 0.54 (s, 6H, TiCH_3). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 142.2, 142.1, 132.5, 132.4, 131.7, 128.6, 128.5, 128.4, 127.7, 126.2 (aromatic carbons), 114.2 (Cp-Carbons), 60.3 (TiCH_3), 50.9 (NCH_2Ph). ^{31}P{^{1}H} NMR (CH_2Cl_2): δ 38.2. Anal. Calcd for $C_{31}H_{29}N_2PTi$: C, 73.47; H, 6.54; N, 5.19. Found: C, 73.68; H, 6.45; N, 5.12.

Cp[Ph$_2$P(*N*-*p*-tolyl)$_2$]ZrMe$_2$, 8c. Method A. Complex **6c** (1.193 g, 1.92 mmol) was placed in a Schlenk flask with toluene (50 mL). Solid MeLi (122 mg, 3.84 mmol, 69% MeLi) was added, and the mixture was stirred for 2 h. The solution was pumped to dryness, and the resulting solid was dissolved in benzene and filtered through Celite. The filtrate was pumped almost to dryness, layered with hexanes, and placed in the freezer overnight to yield a light beige solid (830 mg, 73%). ^{1}H NMR (THF-d_8): δ 7.70−7.42 (br m, 10H, C_6H_5); 6.76 (d, 4H, *m*-$C_6H_4CH_3$, $^3J_{HH}$ = 8.2 Hz), 6.47 (dd, 4H, *o*-$C_6H_4CH_3$, $^3J_{HH}$ = 8.2 Hz, $^4J_{HP}$ = 1.7 Hz), 6.09 (s, 5H, C_5H_5), 2.13 (s, 6H, $C_6H_4CH_3$), 0.03, (s, 6H, ZrCH_3). ^{13}C NMR (C_6D_6): δ 144.8, 133.2−125.8 (C_6H_5 and $C_6H_4CH_3$), 112.4 (C_5H_5), 39.8 (ZrCH_3), 20.5 ($C_6H_4CH_3$). ^{31}P NMR (C_6D_6): δ 35.6. Anal. Calcd for $C_{33}H_{35}N_2PZr$: C, 68.12; H, 6.06; N, 4.81. Found: C, 68.37; H, 6.13; N, 4.73.

Method B. A suspension of $CpZrCl_3$ (1.33 g, 5.07 mmol) in 120 mL of ether was cooled to −65 °C. A solution of MeLi (10.1 mL of 1.54 M in ether, 15.6 mmol) was added to the stirred suspension slowly via syringe over about 30 min. The mixture was allowed to stir for 1 h and 30 min at −65 °C, during which time it became homogeneous. Then Me_3SiCl (2 mL) was added to the reaction mixture in order to quench any excess MeLi. A solution of ligand **2b** (1.70 g, 4.29 mmol) in 50 mL of ether was added slowly via cannula to the reaction mixture at −65 °C over a period of 15 min. The solution was allowed to warm to 25 °C, and then ether and excess Me_3SiCl were removed in vacuo and the solid residue was taken up in 20 mL of toluene and filtered under N_2, washing with additional toluene. The filtrate was concentrated in vacuo to ca. 5 mL, layered with an equal volume of hexane, and then kept at −30 °C to provide a white crystalline solid (1.94 g, 78%).

Cp[Ph$_2$P(*N*-*p*-tolyl)$_2$]TiMe$_2$, 8d. The same procedure described for the preparation of **8b** was followed to synthesize **8d**. Yield: 1.74 g (3.23 mmol, 71%). ^{1}H NMR ($CDCl_3$): δ 7.8−7.5 (20H, phenyl protons), 6.80 (d, 4H, $^3J_{HH}$ = 8.2 Hz), 6.38 (d, 4H, $^3J_{HH}$ = 8.3 Hz), 6.42 (s, 5H Cp-protons), 2.16 (s, 6H, NPhCH_3), 0.65 (s, 6H, TiCH_3). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 145.1, 133.0, 132.8, 132.2, 130.8, 130.6, 129.6, 129.0, 128.6, 128.5, 124.6, 124.4 (aromatic carbons), 114.9 (Cp-carbons), 64.9 (TiCH_3), 20.6 (NPhCH_3). ^{31}P{^{1}H} NMR (CH_2Cl_2): δ 28.4. Anal. Calcd for $C_{31}H_{29}N_2PTi$: C, 73.47; H, 6.54; N, 5.19. Found: C, 73.64; H, 6.48; N, 5.32.

Cp[Ph$_2$P(NSiMe$_3$)$_2$]ZrMe$_2$, 8e. Complex **6d** (1.50 g, 2.56 mmol) was placed in a Schlenk flask with toluene (100 mL). Solid MeLi (163 mg, 5.12 mmol, 69% MeLi) was added, and the mixture was stirred for 2 h. The solution was pumped to dryness, and the resulting solid was dissolved in benzene and filtered through Celite. The filtrate was pumped almost to dryness, layered with hexanes, and placed in the freezer overnight to yield a white solid (1.21 g, 2.21 mmol, 86%). ^{1}H NMR (C_6D_6): δ 7.94−7.87 and 7.15−7.08 (br m, 10H, C_6H_5), 5.42 (s, 5H, C_5H_5), 0.63 (s, 6H, ZrCH_3), −0.12 (s, 18H, SiCH_3). ^{13}C NMR (C_6D_6): δ 132.1, 131.9, and 131.7 (C_6H_5) (other half of signals buried under C_6D_6), 112.4 (C_5H_5), 44.3 (ZrCH_3), 3.35 (SiCH_3). ^{31}P NMR (CH_2Cl_2): δ 24.8. Anal. Calcd for $C_{25}H_{39}PN_2Si_2Zr$: C, 53.00; H, 7.20; N, 5.13. Found: C, 52.86; H, 7.31; N, 4.70.

Cp[Et$_2$P(NSiMe$_3$)$_2$]ZrMe$_2$, 8f. Method A. Complex **6e** (1.00 g, 2.04 mmol) was placed in a Schlenk flask with toluene (100 mL). Solid MeLi (130 mg, 4.08 mmol, 69% MeLi) was added, and the mixture was stirred overnight. The solution was pumped to dryness, and the resulting solid was dissolved in benzene and filtered through Celite. The filtrate was pumped to dryness to yield a white solid (0.800 g, 1.78 mmol, 87%). ^{1}H NMR (C_6D_6): δ 6.25 (s, 5H, C_5H_5), 1.28−1.20 (m, CH_2CH$_3$), 1.02−0.91 (m, CH$_2$CH_3), 0.43 (s, 6H, ZrCH_3), 0.072 (s, 18H, SiCH_3). ^{13}C NMR: δ 112.3 (C_5H_5), 42.6 (ZrCH_3), 25.8 (CH_2CH_3, $^1J_{CP}$ = 65.4 Hz), 5.08 (CH_2CH_3, $^2J_{CP}$ = 6.04 Hz), 3.28 (SiCH_3). ^{31}P NMR (CH_2Cl_2): δ 44.9. Anal. Calcd for $C_{17}H_{39}PN_2Si_2Zr$: C, 45.39; H, 8.74; N, 6.23. Found: C, 45.30; H, 8.81; N, 6.14.

Method B. A suspension of $CpZrCl_3$ (1.34 g, 5.10 mmol) in 120 mL of ether was cooled to −65 °C. A solution of MeLi (10.1 mL of 1.54 M in ether, 15.6 mmol) was added to the stirred suspension slowly via syringe over about 30 min. The mixture was allowed to stir for 1 h and 30 min at −65 °C, during which time it became homogeneous. Then Me_3SiCl (2 mL) was added to the reaction mixture in order to quench any excess MeLi. A solution of ligand **2d** (1.13 g, 4.29 mmol) in 50 mL of ether was added slowly via cannula to the reaction mixture at −65 °C over a period of 15 min. The solution was allowed to warm to 25 °C, and then ether and excess Me_3SiCl were removed in vacuo and the solid residue was taken up in 20 mL of toluene and filtered under N_2, washing with additional toluene. The filtrate was concentrated in vacuo to ca. 5 mL, layered with hexane, and then kept at −30 °C to provide a white crystalline solid (1.45 g, 75%).

Synthesis of Cp*Zr{[(CF$_3$)$_2$C$_6$H$_3$N)]$_2$PPh$_2$}Me$_2$, 8g. Complex **6g** (1.00 g, 1.07 mmol) was placed into a Schlenk flask, and toluene (50 mL) was added at −30 °C. Solid MeLi (68.0 mg, 2.14 mmol, 69% MeLi) was added in small portions to the flask, and the reaction was warmed to room temperature. A pale yellow solution and a white precipitate appeared, and the mixture was stirred overnight. The solvent was then removed in vacuo. The residue was dissolved in two portions of hexane (50 mL × 2) and filtered via Celite to give a pale yellow filtrate. The solvent was then removed in vacuo to ca. 20 mL and placed into a −30 °C freezer to give an off-white solid (0.824 g, 86%). ^{1}H NMR (C_6D_6, ambient): δ 7.66−7.55 and 6.99−6.85 (m, 10H, Ph), 7.33 (s, 2H, ((CF$_3$)$_2$C$_6$H$_3$N)), 7.21 (s, 4H, ((CF$_3$)$_2$C$_6$H$_3$N)), 1.94 (s, 15H, Cp*), 0.28 (s, 6H, CH_3). ^{31}P{^{1}H} NMR (C_6D_6, ambient): δ 37.2 (s). ^{19}F NMR (C_6D_6, ambient): δ −62.9 (s, 12F, CF_3). Anal. Calcd for $C_{40}H_{37}N_2PF_{12}Zr$: C, 53.63; H, 4.16; N, 3.13. Found: C, 54.02; H, 4.22; N, 3.04.

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Supporting Information Available: Crystallographic information files and tables of crystallographic and refinement data, atomic coordinates and isotropic thermal parameters, bond lengths and angles, anisotropic thermal parameters, and H atom coordinates and thermal parameters for complexes **3a**,**b**, **4**, **5b**, **5e**, **7a**, **7b**, and **8d**. This information is available free of charge via the Internet at http://pubs.acs.org.

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