Synthesis of Zirconium Complexes That Contain the Diamidophosphine Ligands $[(Me_3SiNCH_2CH_2)_2PPh]^{2-}$ or $[(RNSiMe_2CH_2)_2PPh]^{2-}$ (R = t-Bu or 2,6-$Me_2C_6H_3$)

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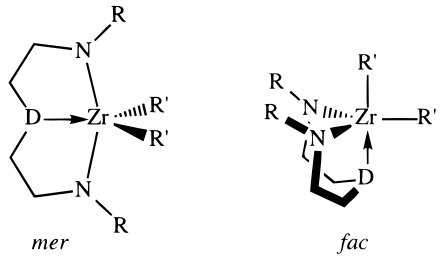
A new synthesis of $PhP(CH_2CH_2NH_3Cl)_2$ is reported that involves the addition of 2 equiv of butyllithium to a mixture of $PhPH_2$ and 2 equiv of $ClCH_2CH_2$(cyclo-$NSiMe_2CH_2CH_2SiMe_2$). The reaction between $PhP(CH_2CH_2NH_3Cl)_2$ and 4 equiv of butyllithium followed by 2 equiv of Me_3SiCl then yielded $(Me_3SiNHCH_2CH_2)_2PPh$ ($H_2[N_2P]$) quantitatively. Addition of $H_2[N_2P]$ to $Zr(NMe_2)_4$ in pentane gave intermediate $[N_2P]Zr(NMe_2)_2$ that was converted without purification to white, crystalline $[N_2P]ZrCl_2$ in 80% yield overall upon treatment with 2 equiv of Me_3SiCl. The alkyl complexes that were prepared include $[N_2P]Zr(THF)MeCl$, $[N_2P]Zr$-(i-Bu)Cl, $[N_2P]ZrMe_2$, $[N_2P]Zr(CH_2Ph)_2$, and $[N_2P]Zr(CH_3)(CH_2Ph)$. An X-ray diffraction study showed that the basic structure of $[N_2P]Zr(CH_3)(CH_2Ph)$ is a distorted trigonal bipyramid in which the methyl group is in the apical position trans to phosphorus and the η^2-benzyl group is cis to phosphorus. Compounds of the type $PhP(CH_2SiMe_2NHR)_2$ (R = t-Bu or 2,6-$Me_2C_6H_3$; $H_2[R_2NPN]$) were prepared by treating $ClCH_2SiMe_2Cl$ with LiNHR to give $ClCH_2$-$SiMe_2NHR$ followed by a reaction between $PhPH_2$, $ClCH_2SiMe_2NHR$, and butyllithium. Zirconium complexes that were prepared include $[t\text{-}Bu_2NPN]ZrMeCl$, $[Ar_2NPN]ZrMeCl$, and $[Ar_2NPN]ZrMe_2$. An attempted synthesis of $[t\text{-}Bu_2NPN]ZrMe_2$ led to loss of a *tert*-butyl group and formation of a dimeric complex containing imido-type bridging nitrogen ligands, as confirmed in an X-ray study. X-ray studies of $[t\text{-}Bu_2NPN]ZrMeCl$ and $[Ar_2NPN]ZrMeCl$ demonstrate that extensive steric crowding exerted by a *tert*-butyl group in complexes of this type contributes to the inability to form a simple complex such as $[PhP(CH_2SiMe_2N\text{-}t\text{-}Bu)_2]ZrMe_2$.

Introduction

Several types of "diamido/donor" ligands have been synthesized in the last several years and employed in the synthesis of early transition metal complexes.[1−15] Multidentate ligands of this type that have a central donor atom, which is the more common type, and "arms" that contain two atoms between the donor and the amido nitrogen atom have considerable potential as ligands in organometallic chemistry. An example is the $[(t\text{-}BuN\text{-}o\text{-}C_6H_4)_2O]^{2-}$ ($[NON]^{2-}$) ligand, zirconium complexes of which have been found to be catalysts for the living polymerization of 1-hexene.[5,6] Diamido/donor ligands that contain nitrogen as the central donor include $[(Me_3SiNCH_2CH_2)_2NSiMe_3]^{2-}$ [1−4] and $[(C_6F_5NCH_2$-$CH_2)_2NH]^{2-}$.[8] One of the issues surrounding group 4



complexes that contain diamido/donor ligands is whether the geometries of five-coordinate dialkyl complexes (*mer* and *fac* being the ideal limiting geometries where D = donor) can be correlated with the degree of living character of cationic pseudotetrahedral catalysts in the

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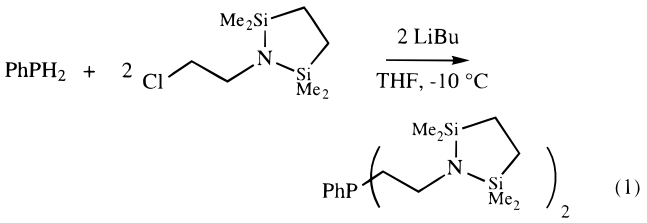
polymerization of ethylene and terminal olefins. Consequently we became interested in attempting to force the geometry of a five-coordinate species to be *fac* by employing phosphorus as the donor. No complex that contains a simple diamido/phosphine ligand has been reported, even though $PhP(CH_2CH_2NH_3Cl)_2$, the precursor to $PhP(CH_2CH_2NH_2)_2$ and possible $PhP(CH_2CH_2NHR)_2$ species, was prepared over 30 years ago.[16] Ligands that are most closely related to $[R'P(CH_2CH_2NR)_2]^{2-}$ ligands include aminodiphosphine ligands[17,18] such as $(Ph_2PCH_2SiMe_2)_2NH$ and a related macrocyclic dianionic diamidodiphosphine ligand, $[N(SiMe_2CH_2P(Ph)CH_2SiMe_2)_2N]^{2-}$.[19] We report here the synthesis of two types of diamido/phosphine ligands, $[PhP(CH_2CH_2NSiMe_3)_2]^{2-}$ ($[N_2P]^{2-}$) and $[PhP(CH_2SiMe_2NR)_2]^{2-}$ (R = t-Bu or R = 2,6-$Me_2C_6H_3$ = Ar; $[R_2NPN]^{2-}$) and several zirconium complexes that contain them.[20]

Results and Discussion

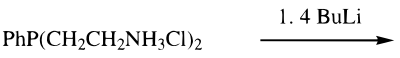
The $[PhP(CH_2CH_2NSiMe_3)_2]^{2-}$ Ligand and $[N_2P]$-Zr Complexes. We decided to construct the first ligand from the known molecule,[16] $PhP(CH_2CH_2NH_3Cl)_2$. The synthesis of $PhP(CH_2CH_2NH_3Cl)_2$ that is reported in the literature (in 23% yield) consists of the treatment of $ClCH_2CH_2NH_2$ with $NaP(Ph)CH_2CH_2NH_2$ in liquid ammonia. We believe a more convenient preparation is that shown in eq 1. This synthesis is related to that employed



(1)

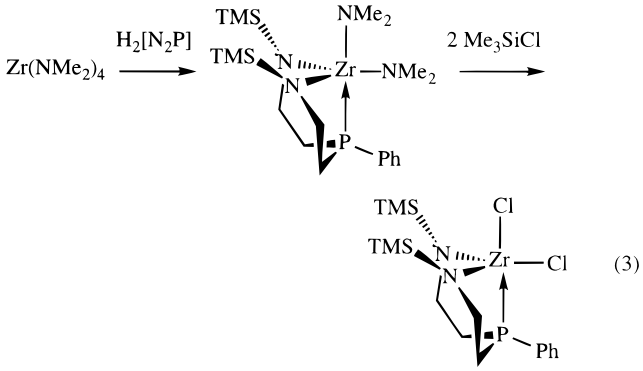
by Fryzuk to prepare $(Ph_2PCH_2SiMe_2)_2NH$ and $HN(SiMe_2CH_2P(Ph)CH_2CH_2)_2NH$.[19] This approach avoids making and handling phosphides and liquid ammonia as a solvent, and yields are essentially quantitative. The product is obtained as a light yellow oil on a large scale (~50 g). $PhP(CH_2CH_2NH_3Cl)_2$ is obtained by treating $PhP[CH_2CH_2(cyclo\text{-}NSiMe_2CH_2CH_2SiMe_2)]_2$ in ether with aqueous HCl.

The easiest amido derivatives to prepare are those that contain trimethylsilyl groups. The reaction between $PhP(CH_2CH_2NH_3Cl)_2$ and 4 equiv of butyllithium followed by 2 equiv of Me_3SiCl yielded $(Me_3SiNHCH_2CH_2)_2PPh$ essentially quantitatively (eq 2). A white, pentane-soluble, crystalline dilithium salt, $Li_2[N_2P]$ ($[N_2P]^{2-}$ = $[(Me_3SiNCH_2CH_2)_2PPh]^{2-}$), could be prepared in moderate yield by treating $(Me_3SiNHCH_2CH_2)_2PPh$ with 2 equiv of butyllithium.



(2)

Addition of $H_2[N_2P]$ to $Zr(NMe_2)_4$ in pentane gave intermediate $[N_2P]Zr(NMe_2)_2$ as an oil that was converted without purification to white, crystalline $[N_2P]ZrCl_2$ in 80% yield overall upon treatment with 2 equiv of Me_3SiCl (eq 3). In crude $[N_2P]Zr(NMe_2)_2$ methyl resonances for the two amido groups (each with equivalent methyl groups on the NMR time scale) are found at 3.13 and 3.05 ppm in the proton NMR spectrum, and the molecule contains a plane of symmetry. The phosphorus resonance is found at −10.5 ppm in the ^{31}P NMR spectrum. NMR data for $[N_2P]ZrCl_2$ are also consistent with a structure that has mirror symmetry; the phosphorus resonance is found in the ^{31}P NMR spectrum at 1.94 ppm. On the basis of X-ray studies of related species reported below we presume that both molecules have *fac* geometries (eq 3). However, we cannot discount the possibility that $[N_2P]ZrCl_2$ is a mirror symmetric dimer (in the solid state) that has two pseudooctahedral zirconium centers connected by two bridging chlorides and the phosphorus donors on opposite sides of the $Zr_2(\mu\text{-}Cl)_2$ ring.



(3)

Monoalkyl complexes can be prepared by monoalkylation of $[N_2P]ZrCl_2$ (eq 4). When MeMgCl (in THF) is added to $[N_2P]ZrCl_2$ in ether, $[N_2P]Zr(THF)MeCl$ is obtained in ~40% yield as pentane-soluble white crystals. The proton NMR spectrum revealed a doublet

$$[N_2P]ZrCl_2 \xrightarrow{\text{monoalkylation}} [N_2P]ZrRCl \qquad (4)$$
$$R = CH_3,\ CH_2CHMe_2$$

resonance for the methyl group at 0.84 ppm with $^2J_{HP}$ = 7 Hz. As we will show later, a PH coupling on the order of 7 Hz is indicative of the methyl group being in a position cis to the phosphine. A complex that does not contain THF could be prepared by employing Me_2Mg in ether. However, several attempts to obtain satisfactory analytical data for $[N_2P]ZrMeCl$ failed, even though NMR spectra were unambiguous. Proton NMR spectra of $[N_2P]ZrMeCl$ revealed a singlet resonance for the methyl group at 0.9 ppm (undetectable J_{HP}), which on the basis of data presented below we believe to be characteristic of a methyl group trans to the phosphorus donor. This molecule could be a dimer with a pseudooctahedral arrangement about each Zr and two bridging chlorides. The analogous isobutyl complex, $[N_2P]Zr(i\text{-}$

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Table 1. Crystallographic Data, Collection Parameters, and Refinement Parameters for $[N_2P]Zr(CH_3)(CH_2Ph)$, $[t\text{-}Bu_2NPN]Zr(CH_3)Cl$, $[Ar_2NPN]Zr(CH_3)Cl$, and $\{[t\text{-}BuNSiMe_2CH_2P(Ph)CH_2SiMe_2N]Zr(CH_3)\}_2$ ("Dimer")

	$[N_2P]Zr(CH_3)(CH_2Ph)$	$[t\text{-}Bu_2NPN]Zr(CH_3)Cl$	$[Ar_2NPN]Zr(CH_3)Cl$	Dimer
empirical formula	$C_{24}H_{41}N_2PSi_2Zr$	$C_{21}H_{42}ClN_2PSi_2Zr$	$C_{29}H_{42}ClN_2PSi_2Zr$	$C_{34}H_{66}N_4P_2Si_4Zr_2$
fw	535.96	536.39	632.47	887.65
cryst dimens (mm)	0.26 × 0.12 × 0.08	0.49 × 0.35 × 0.28	0.35 × 0.33 × 0.23	0.25 × 0.20 × 0.08
cryst syst	monoclinic	orthorhombic	monoclinic	triclinic
a (Å)	13.677(3)	11.12570(10)	17.201(4)	10.8271(4)
b (Å)	11.936(3)	13.331	18.766(4)	11.6428(4)
c (Å)	17.646(3)	18.2853(3)	20.187(5)	19.1805(7)
α	90	90	90	97.9570(10)
β (deg)	96.182(14)	90	90	92.1900(10)
γ	90	90	90	111.7450(10)
V (Å^3)	2863.9(11)	2712.02(5)	6516(3)	2213.63(14)
space group	$P2_1/c$	$P2_12_12_1$	$P2/c$	$P\bar{1}$
Z	4	4	8	2
ρ_{calc} (Mg/m^3)	1.243	1.314	1.289	1.332
abs coeff (mm^{-1})	0.536	0.661	0.562	0.679
F_{000}	1128	1128	2640	928
temp (K)	183(2)	183(2)	153(2)	163(2)
θ range for data collection (deg)	1.50−23.26	1.89−23.26	1.90−23.26	1.91−23.26
no. of reflns collected	8939	11176	11580	9111
no. of ind reflns	3928	3888	3546	6223
R [$I > 2\sigma(I)$]	0.0450	0.0175	0.0606	0.0522
R_w [$I > 2\sigma(I)$]	0.0912	0.0476	0.1600	0.1173
GoF	1.164	1.084	1.140	1.105
extinction coeff	0.0016 (3)	0.0094(4)	0.0021(3)	0.0023
largest diff peak and hole (e Å^{-3})	0.373 and −0.332	0.270 and −0.263	0.825 and −0.399	1.279 and −0.833

Bu)Cl, was also prepared in good yield and analyzed satisfactorily. In this case J_{HP} (7.7 Hz) for the isobutyl methylene group was more consistent with the isobutyl group being in a position cis to the phosphorus in a monomeric, five-coordinate *fac* species.

Dialkyl complexes can be prepared by dialkylation of $[N_2P]ZrCl_2$ (eq 5). Addition of 2 equiv of MeMgCl to

$$[N_2P]ZrCl_2 \xrightarrow{\text{dialkylation}} [N_2P]Zr(R_1)(R_2) \quad (5)$$
$$R_1 = R_2 = CH_3,\ CH_2Ph;\quad R_1 = CH_3,\ R_2 = CH_2Ph$$

$[N_2P]ZrCl_2$ yielded $[N_2P]ZrMe_2$ in high yield. Although NMR data suggest that this complex is quite pure, it resisted crystallization and therefore could not be purified and analyzed. $[N_2P]Zr(^{13}CH_3)_2$ was prepared similarly. Proton NMR spectra of $[N_2P]ZrMe_2$ reveal a doublet resonance at 0.80 ppm for one methyl group ($^2J_{HP} = 6$ Hz) and a singlet resonance at 0.60 ppm for the other methyl group with no detectable coupling of the methyl protons to phosphorus. Carbon NMR data reveal methyl resonances with dramatically different $^2J_{CP}$ values at 35.9 ($^2J_{CP} = 29$ Hz) and 40.9 ppm ($^2J_{CP} = 2$ Hz). An analogous $[N_2P]Zr(CH_2Ph)_2$ complex could be prepared similarly and analyzed satisfactorily. Proton NMR data reveal benzyl methylene resonances at 2.75 ppm ($J_{HP} = 6.6$ Hz) and 2.69 ppm ($J_{HP} = 2.4$ Hz), while the methylene carbon atom resonances in the carbon NMR spectrum of $[N_2P]Zr(CH_2Ph)_2$ are found at 69.3 ppm ($^2J_{CP} = 3.2$ Hz, $^1J_{CH} = 126$ Hz) and 65.9 ppm ($^2J_{CP} = 22$ Hz, $^1J_{CH} = 118$ Hz). Finally, $[N_2P]Zr(^{13}CH_3)(CH_2Ph)$ could be prepared and isolated in good yield by treating $[N_2P]ZrCl_2$ first with $^{13}CH_3MgI$ and then with $PhCH_2MgCl$. The proton and carbon CH_2 resonances for the benzyl ligand were found at 2.82 ppm ($^3J_{HP} = 9$ Hz) and 62.4 ppm ($^2J_{CP} = 4.6$ Hz), respectively, while for the methyl group they were found at 0.59 ppm (undetectable J_{HP}) and 38.2 ppm ($^2J_{CP} = 27.9$ Hz), respectively. Therefore the benzyl ligand has the larger value for $^3J_{HP}$ (∼10 Hz) and the smaller value for $^2J_{CP}$ (∼5 Hz), while the methyl ligand has a small (unobservable) $^3J_{HP}$ and the larger value for $^2J_{CP}$ (28 Hz).

An X-ray diffraction study (Tables 1 and 2) verified that the basic structure of $[N_2P]Zr(CH_3)(CH_2Ph)$ is a distorted trigonal bipyramid, that the methyl group is in the apical position trans to phosphorus, and that the benzyl ligand is in the "equatorial" position and bound in an η^2 manner (Figure 1). Therefore we can conclude that the large value for $^2J_{CP}$ and small (undetectable) value for $^3J_{HP}$ are associated with the alkyl group trans to the phosphine donor (methyl), while the small value for $^2J_{CP}$ and a large value for $^3J_{HP}$ are associated with the alkyl group cis to the phosphine donor (benzyl). The Zr−C(41) distance (2.835(4) Å) and Zr−C(47)−C(41) angle (95.4(2)°) are similar to distances and angles in several other recently characterized η^2-benzyl complexes of zirconium,[21−25] while the Zr−P distance (2.9343(11) Å) is somewhat longer than what has been observed (typically 2.75−2.85 Å) in a variety of zirconium phosphine complexes.[19,26−43] The $Zr-N_{amido}$ bond lengths also

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Table 2. Selected Distances and Angles in $[N_2P]Zr(CH_3)(CH_2Ph)$, $[t\text{-}Bu_2NPN]Zr(CH_3)Cl$, $[Ar_2NPN]Zr(CH_3)Cl$, and $\{[t\text{-}BuNSiMe_2CH_2P(Ph)CH_2SiMe_2N]Zr(CH_3)\}_2$ ("Dimer")

	$[N_2P]Zr(CH_3)(CH_2Ph)$	$[t\text{-}Bu_2NPN]Zr(CH_3)Cl$	$[Ar_2NPN]Zr(CH_3)Cl$	Dimer (Zr(1))	Dimer (Zr(2))
$Zr-L_{ax}$	2.294(4)	2.5067(6)	2.715(3)	2.098(5)	2.112(5)
$Zr-L_{eq}$	2.295(4)	2.278(2)	2.343(8)	2.282(6)	2.272(6)
Zr−N(1)	2.054(3)	2.093(2)	2.093(5)	2.101(5)	2.113(5)
Zr−N(2)	2.062(3)	2.116(2)	2.110(5)	2.126(4)	2.139(5)
Zr−P	2.9343(1)	2.6797(6)	2.916(2)	2.820(2)	2.774(2)
$L_{ax}-Zr-N(1)$	109.96(14)	133.09(5)	105.1(2)	82.2(2)	81.6(2)
$L_{ax}-Zr-N(2)$	105.1(2)	95.87(5)	105.0(2)	116.9(2)	117.7(2)
$L_{ax}-Zr-L_{eq}$	96.5(2)	84.57(6)	93.8(2)	101.3(2)	102.1(2)
$L_{ax}-Zr-P$	174.65(12)	146.37(2)	179.44(6)	154.67(13)	154.53(13)
N(1)−Zr−N(2)	102.35(13)	112.41(7)	122.3(2)	116.2(2)	117.4(2)
$N(1)-Zr-L_{eq}$	114.25(14)	105.29(8)	109.1(2)	120.5(2)	120.0(2)
N(1)−Zr−P	72.89(9)	79.81(5)	74.9(2)	73.29(13)	73.64(13)
$N(2)-Zr-L_{eq}$	127.56(13)	126.00(8)	116.6(2)	114.2(2)	113.0(2)
N(2)−Zr−P	69.70(8)	71.94(5)	74.6(2)	80.59(13)	79.85(13)
C−P−C	106.7(2)	106.99(11)	106.3(3)	105.1(3)	104.2(3)
$Zr-P-C_{ipso}$	144.66(13)	125.07(8)	128.8(3)	133.0(2)	129.8(2)
P−Zr−N(1)−X	139.6	147.5	178.2	173.1	172.6
P−Zr−N(2)−X	144.7	148.9	151.9	155.4	153.9
Zr−N(1)−X	125.0(2)	116.02(13)	108.6(4)	116.2(4)	116.3(4)
Zr−N(2)−X	122.6(2)	121.08(14)	113.4(5)	96.5(2)	96.6(2)
N(1),Zr,P,N(2) planes	111	118	130	121	123
"arm lengths"	6.912, 6.921	7.553, 7.567	7.546, 7.574	7.573, 7.550	7.555, 7.568
Zr−C(47)−C(41)	95.4(2)				
Zr−C(41)	2.835(4)				

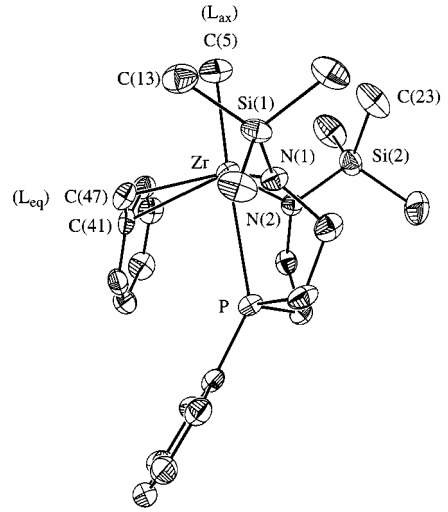

Figure 1. ORTEP drawing of the structure of $[(Me_3SiNCH_2CH_2)_2P]Zr(CH_3)(CH_2Ph)$.

are typical of those in related diamido compounds in the literature, which usually fall in the range 2.05−2.12 Å.[1,5,13,15,44−46] The Zr is situated above the C(47)−N(2)−N(1) plane, with the sum of the angles at the "equatorial" ligands (N(1), N(2), and C(47)) being 344°. However, the C(47)−Zr−N(2) angle (127.56(13)°) is the largest of the three, presumably in order to accommodate the η^2-benzyl ligand that points toward N(2). The sum of the angles around N(1) (360.0°) and N(2) (359.8°) suggests that the amido nitrogen atoms are strictly planar, as is the case in all compounds whose structures are reported here. However, the TMS groups are "tipped" from a "vertical" position (with P−Zr−N−Si dihedral angles = 139.6° and 144.7°), presumably in order to avoid interacting with C(5), the consequence of which is an "envelope" configuration in the PC_2NZr five-membered rings. The TMS group containing Si(2) points between the two imido nitrogen atoms (away from the η^2 benzyl ligand), and Si(1) points away from Si(2). The Zr−N−Si angles (125.0(2)° and 122.6(2)°) are approximately the same as those observed in a wide variety of triamidoamine complexes (~125°).[47] A convenient measure of the trigonal nature of the equatorial ligand set is the angle between the N(1)/Zr/P and N(2)/Zr/P planes, which here is 111°. This angle and the N(1)−Zr−N(2) angle are the smallest of any corresponding angles in related complexes reported here, we presume in response to the steric demands of the η^2-benzyl ligand and formation of what could be called a pseudo six-coordinate geometry.

We were especially interested in whether $[N_2P]ZrMe_2$ could be activated to yield a "cation" (in the presence of a "weakly coordinating" anion) that would be active for polymerization of terminal olefins.[48,49] $[N_2P]Zr(^{13}CH_3)_2$ reacts with $[Ph_3C][B(C_6F_5)_4]$ in bromobenzene-d_5 at −30

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°C. The ^{13}C NMR spectrum at −30 °C shows a peak at 55.1 ppm (14 ppm downfield from the lower field methyl resonance in $[N_2P]Zr(^{13}CH_3)_2$) which we assign to "$\{[N_2P]Zr(^{13}CH_3)\}^+$" (with solvent and/or anion associated with it) as well as a resonance for $Ph_3C^{13}CH_3$, the expected product of methyl abstraction or oxidative cleavage, at 30.5 ppm. The ^{31}P NMR spectrum shows a relatively broad resonance at 26.8 ppm, 42.5 ppm downfield of the ^{31}P resonance in $[N_2P]ZrMe_2$. No resonance for the methyl group in the proton NMR spectrum of $\{[N_2P]Zr(^{13}CH_3)\}^+$ could be identified unambiguously, however. Evidence of decomposition is observed by ^{13}C and ^{31}P NMR within minutes after warming the sample to room temperature. Similar results were obtained upon treating $[N_2P]Zr(CH_2Ph)_2$ with $[Ph_3C][B(C_6F_5)_4]$ under similar conditions. When 20 equiv of 1-hexene were added to "$\{[N_2P]Zr(CH_3)\}[B(C_6F_5)_4]$" in bromobenzene-$d_5$ and the reaction was held at 0 °C for 1 h, some poly(1-hexene) formed, according to ^1H NMR spectra, although >50% of the initial 1-hexene was still present. Longer reaction times yielded little additional poly(1-hexene). We conclude that while "$\{[N_2P]Zr(^{13}CH_3)\}^+$" *may* be formed at 0 °C or below, it is not stable enough to be an initiator for the controlled polymerization of 1-hexene under the conditions employed.

The $[R_2NPN]^{2-}$) Ligand and $[R_2NPN]Zr$ Complexes (R = t-Bu or 2,6-$Me_2C_6H_3$). We hypothesized that the instability of zirconium alkyl cations containing the $[N_2P]^{2-}$ ligand might be ascribed to some adverse reaction involving the trimethylsilyl substituent on the amido nitrogen atoms (e.g., CH activation or cleavage of the Si−N bond). For this reason we turned to the synthesis of diamido/phosphine ligands in which a dimethylsilyl group is incorporated into the backbone and an alkyl (t-Bu) or aryl (2,6-$Me_2C_6H_3$) substituent is present as an "external" substituent on the amido nitrogen atoms. (The *tert*-butyl group has been used successfully in $[NON]^{2-}$ complexes[5,6] and 2,6-disubstituted aryl groups in complexes containing the $[(ArylNCH_2CH_2)_2O]^{2-}$ ligand.[7,15]) The potential advantage of incorporating a dimethylsilyl group into the backbone is that the metal will not have ready access to the CH bonds in the silyl methyl groups in an intramolecular reaction, and a variety of substituents on nitrogen in theory could be employed.

The syntheses again are fashioned after those of amidodiphosphine ligands[17,18] and $H_2[N_2P]$ described above. The *tert*-butyl derivative can be prepared readily as shown in eqs 6 and 7. The H_2[t-Bu_2NPN] compound

$$ClCH_2SiMe_2Cl + 2.1\ t\text{-}BuNH_2 \xrightarrow{\text{ether}} ClCH_2SiMe_2NH\text{-}t\text{-}Bu \quad (6)$$

$$2\ ClCH_2SiMe_2NH\text{-}t\text{-}Bu + PhPH_2 \xrightarrow[\text{ether}]{2.1\ LiBu} PhP(CH_2SiMe_2NH\text{-}t\text{-}Bu)_2 \quad (7)$$

shown in eq 7 is isolated as a pale yellow oil in nearly quantitative yield. Deprotonation with butyllithium in pentane yields Li$_2$[t-Bu_2NPN], which reacts with $ZrCl_4(THF)_2$ in diethyl ether to yield colorless, crystalline [t-Bu_2NPN]$ZrCl_2$ in 64% yield. Proton and carbon NMR spectra of [t-Bu_2NPN]$ZrCl_2$ are consistent with a pseudo trigonal bipyramidal complex containing a mirror plane,

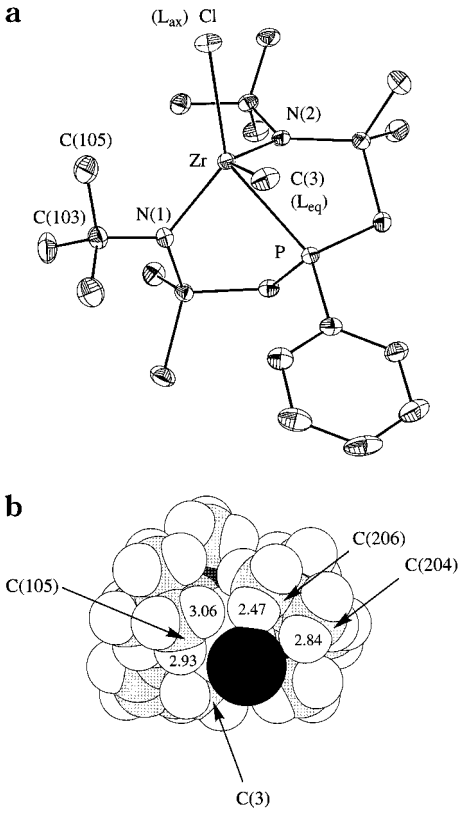


Figure 2. (a) ORTEP drawing of the structure of [(t-BuNSi$Me_2CH_2)_2$P]Zr(CH_3)Cl. (b) Top view of Chem 3D space-filling drawing of the structure of [(t-BuNSi$Me_2CH_2)_2$P]Zr-(CH_3)Cl (including protons).

although it is possible that this species is a dimer with bridging chlorides.

Addition of 1 equiv of LiMe to [t-Bu_2NPN]$ZrCl_2$ yields [t-Bu_2NPN]ZrMeCl in good yield. The methyl ligand appears to be located in the equatorial position on the basis of the magnitude of $^3J_{HP}$ (11 Hz) for the methyl resonance at 0.58 ppm in the proton NMR spectrum. An X-ray study of [t-Bu_2NPN]ZrMeCl showed this to be the case (Tables 1 and 2, Figure 2). However, the trigonal bipyramid is severely distorted (Figure 2a) in that the "axial" chloride has been "pushed" from the "ideal" axial position by the *tert*-butyl group containing C(103), and in particular the methyl group bound to it (C(105)), as judged from the P−Zr−Cl angle of only 146.37(2)°. A top view of a space-filling drawing (Figure 2b) reveals that the chloride has taken the only position possible from a steric point of view, i.e., the apical chloride is 3.50 Å from C(105), 3.46 Å from C(206), and 3.73 Å from C(204), and contacts with four surrounding methyl protons range from 2.47 to 3.06 Å. Interactions of this magnitude between the TMS methyl groups and the apical methyl group on Zr are also found in $[N_2P]Zr(CH_3)(CH_2Ph)$ (e.g., C(5)···C(23) = 3.50 Å and C(5)···C(13) = 3.52 Å). The Zr−N(1)−C(103) angle in [t-Bu_2NPN]ZrMeCl is ∼9° smaller than the corresponding angle in $[N_2P]Zr(CH_3)(CH_2Ph)$, which should contribute to greater steric problems in terms of accommodating the chloride ligand in the ideal apical position. The Zr−P bond is shorter and the Zr−P−C_{ipso} bond angle is also significantly smaller in [t-Bu_2NPN]ZrMeCl than in $[N_2P]Zr(CH_3)(CH_2Ph)$. One readily quantifiable

difference between $[N_2P]Zr(CH_3)(CH_2Ph)$ and [t-Bu_2-NPN]ZrMeCl is the length of the "arms" between P and Zr. The average of the sum of the four distances in the "arms" in [t-Bu_2NPN]ZrMeCl (7.560 Å) is significantly greater than that in $[N_2P]Zr(CH_3)(CH_2Ph)$ (6.917 Å), primarily as a consequence of the larger size of Si versus C. In the end, however, we can simply point to the greater steric demand of a *tert*-butyl group near the metal as perhaps the most important difference in steric crowding between $[N_2P]Zr(CH_3)(CH_2Ph)$ and [t-Bu_2-NPN]ZrMeCl and the reason the chloride ligand cannot occupy the axial position in [t-Bu_2NPN]ZrMeCl.

One of the advantages of the $[R_2NPN]^{2-}$ ligand is the ability to vary the R group. For example, we could readily prepare the 2,6-$Me_2C_6H_3$ (Ar) derivative. The Ar group was chosen on the basis of its relatively planar form and in anticipation therefore that the structure of $[Ar_2NPN]ZrMeCl$ would not show the dramatic steric interaction that pushed the axial chloride from the axial position in [t-Bu_2NPN]ZrMeCl. $H_2[Ar_2NPN]$ was prepared by reactions analogous to those used to prepare H_2[t-Bu_2NPN], and $[Ar_2NPN]ZrMe_2$ was prepared by the route shown in eq 8. It is interesting to note that

$$Zr(NMe_2)_4 \xrightarrow[-2\ Me_2NH]{H_2[Ar_2NPN]} [Ar_2NPN]Zr(NMe_2)_2$$

$$\xrightarrow[-2\ Me_2NH]{2\ HCl} [Ar_2NPN]ZrCl_2 \xrightarrow{2\ MeMgCl} [Ar_2NPN]ZrMe_2 \quad (8)$$

the ligand is not cleaved off upon addition of HCl to $[Ar_2$-$NPN]Zr(NMe_2)_2$, presumably as a consequence of the multidentate nature of the $[Ar_2NPN]^{2-}$ ligand. Even if a proton adds to the amido nitrogen of the $[Ar_2NPN]^{2-}$ ligand instead of the dimethylamido ligand it must be transferred to the dimethylamido ligand, before further protonations or ligand degradation reactions result in decomposition. Addition of only 1 equiv of MeMgCl to $[Ar_2NPN]ZrCl_2$ leads to a mixture of $[Ar_2NPN]ZrMe_2$ and $[Ar_2NPN]ZrMeCl$. $[Ar_2NPN]ZrMeCl$ could be crystallized from a CH_2Cl_2/pentane mixture at −35 °C to afford colorless crystals of X-ray crystallography quality in 30% yield. NMR spectra of both $[Ar_2NPN]ZrMe_2$ and $[Ar_2NPN]ZrMeCl$ are fully consistent with the expected *fac* structures. Proton NMR data suggest that the methyl group in $[Ar_2NPN]ZrMeCl$ is in an equatorial position ($^3J_{HP}$ = 8.8 Hz), while in $[Ar_2NPN]ZrMe_2$ J_{HP} values for the methyl groups are 6.6 and 1.5 Hz in what we presume to be Me_{eq} and Me_{ax}, respectively.

An X-ray study of $[Ar_2NPN]ZrMeCl$ showed it to be a trigonal bipyramidal species in which the apical chloride is strictly trans to the phosphorus donor (Tables 1 and 2; Figure 3), as judged by the Cl−Zr−P angle of 179.44-(6)°. Interestingly, the Zr−Cl distance in $[Ar_2NPN]$-ZrMeCl (2.715(3) Å) is ∼0.2 Å longer than the Zr−Cl distance in [t-Bu_2NPN]ZrMeCl, perhaps as a consequence of the chloride being strictly trans to the P donor. The Zr−P distance is similar to what it is in $[N_2P]Zr$-$(CH_3)(CH_2Ph)$ rather than [t-Bu_2NPN]ZrMeCl. One of the Ar groups is virtually "upright", as judged by the P−Zr−N(1)−C angle of 178.2°, while the other is tipped to a significant degree (P−Zr−N(2)−C = 151.9°). Consequently the Zr−N(1)−C angle is only 108.6(4)°, while Zr−N(2)−C = 113.4(5); both are the smallest of the Zr−N−X angles in $[N_2P]Zr(CH_3)(CH_2Ph)$, [t-Bu_2NPN]-

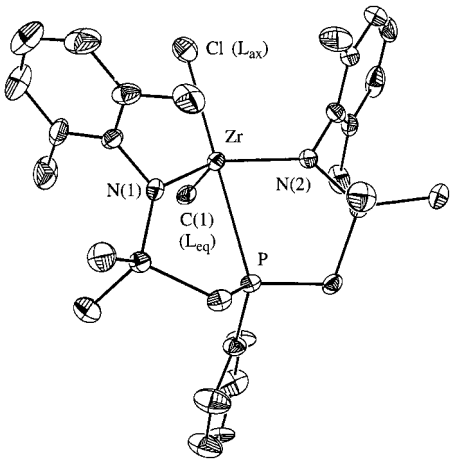
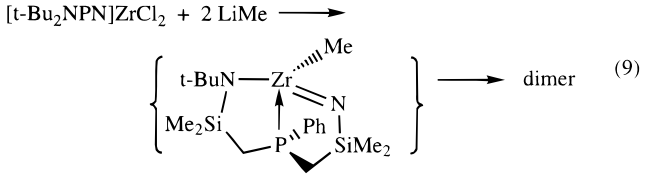


Figure 3. ORTEP drawing of the structure of [(2,6-$Me_2C_6H_3NSiMe_2CH_2)_2P]Zr(CH_3)Cl$.

ZrMeCl, and $[Ar_2NPN]ZrMeCl$. The Zr−P−C_{ipso} angle is similar to what it is in [t-Bu_2NPN]ZrMeCl; indeed, the C−P−C angle is virtually invariant in $[N_2P]Zr(CH_3)$-(CH_2Ph), [t-Bu_2NPN]ZrMeCl, and $[Ar_2NPN]ZrMeCl$. The sum of the four distances in the ligand "arms" in $[Ar_2NPN]ZrMeCl$ are virtually the same as in [t-Bu_2-NPN]ZrMeCl. The steric problems in the apical pocket in [t-Bu_2NPN]ZrMeCl clearly are not present in $[Ar_2$-NPN]ZrMeCl. The reason is most likely primarily the planar nature of the Ar groups on the amido donors in contrast to the spherical, sterically unyielding nature of a *tert*-butyl group.

Addition of 2 equiv of MeMgCl or LiMe to [t-Bu_2NPN]-$ZrCl_2$ (or 1 equiv to [t-Bu_2NPN]ZrMeCl) yields complex mixtures in which there is no evidence for [t-Bu_2NPN]-$ZrMe_2$, according to NMR spectra. When methyllithium was employed, a product could be isolated in ∼25% yield that contains only *one tert*-butyl group (eq 9). The ^{1}H



NMR spectrum of this product in C_6D_6 is consistent with a compound that has no symmetry about zirconium and one "equatorial" methyl ligand (δ = 0.87 ppm with $^3J_{HP}$ = 10 Hz). An X-ray study showed this product to be a dimer of the imido complex, "[t-BuNSiMe_2CH_2P(Ph)CH_2-$SiMe_2$N]ZrMe", in which the imido nitrogen is bridging between two Zr centers to yield a $Zr_2(\mu$-$N)_2$ ring (Tables 1 and 2; Figure 4). We hypothesize that electron transfer to Zr followed by loss of chloride ion and a *tert*-butyl radical leads to "[t-BuNSiMe_2CH_2P(Ph)CH_2SiMe_2N]-ZrMe", which then dimerizes to give the observed product. Evidently steric crowding prevents nucleophilic displacement of the chloride in [t-Bu_2NPN]ZrMeCl, or the distorted structure of [t-Bu_2NPN]ZrMeCl makes it more susceptible to electron transfer, or both. No method of isolating any other product of the reaction between [t-Bu_2NPN]$ZrCl_2$ and 2 equiv of MeMgCl or LiMe has been found.

The structure of {[t-BuNSiMe_2CH_2P(Ph)CH_2SiMe_2N]-$ZrMe\}_2$ cannot be compared directly with the structures

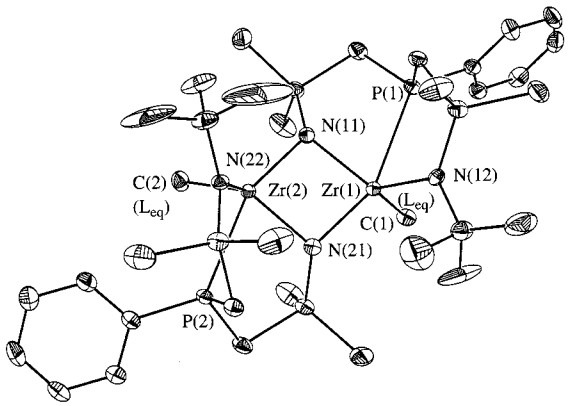


Figure 4. ORTEP drawing of the structure of {[t-Bu-NSiMe$_2$CH$_2$P(Ph)CH$_2$SiMe$_2$N)Zr(CH$_3$)}$_2$.

of [N$_2$P]Zr(CH$_3$)(CH$_2$Ph), [t-Bu$_2$NPN]ZrMeCl, and [Ar$_2$-NPN]ZrMeCl as a consequence of the restrictions imposed by the formation of the Zr$_2$(μ-N)$_2$ ring in the dimer, i.e., the "axial" ligand for each Zr is now the "imido" donor from the other half of the molecule, and the trigonal bipyramidal geometry about each Zr is consequently distorted. The L$_{ax}$−Zr−P angles are restricted to ∼155° and a measure of the "steric pressure" at the apical position therefore is not possible. The Zr(1)−N(11) and Zr(2)−N(21) bond lengths are similar to Zr−N(amido) bond lengths in other molecules discussed here, while the Zr−P distances and the Zr−P−C$_{ipso}$ angles are similar to those in [t-Bu$_2$NPN]ZrMeCl and [Ar$_2$NPN]ZrMeCl. Other distances and angles can be found in Table 2 and will not be discussed in any detail.

The reaction between [Ar$_2$NPN]ZrMe$_2$ and [Ph$_3$C][B(C$_6$F$_5$)$_4$] in bromobenzene or chlorobenzene at −30 °C afforded a mixture of different species, according to ^{31}P NMR spectra. More complex mixtures were formed upon warming the sample to −20 °C. Attempts to prepare a cationic dimethylamine adduct by protonating a methyl ligand in [Ar$_2$NPN]ZrMe$_2$ with [PhNMe$_2$H][B(C$_6$F$_5$)$_4$] also gave mixtures of unstable species. [Ar$_2$NPN]ZrMe$_2$ in bromobenzene-d_5 was activated by addition of [Ph$_3$C][B(C$_6$F$_5$)$_4$] at −35 °C and the solution was kept at 0 °C for 30 min. Addition of several equivalents of 1-hexene resulted in incomplete polymerization, as evidenced by ^{1}H NMR. The ^{1}H NMR spectrum also showed broad olefinic resonances, which suggests that β-hydride elimination occurs during the polymerization. We conclude that cationic species formed from [Ar$_2$NPN]ZrMe$_2$ are not stable under the conditions employed and not adequate as initiators for polymerization of 1-hexene under the conditions employed.

Conclusions

The ligands reported here have a "fixed" geometry that imposes some significant steric pressure on the apical coordination site, the degree of which depends markedly on the nature of the amido substituent and follows the order Ar < SiMe$_3$ ≪ t-Bu. This "fixed" *fac* geometry consequently in theory would allow the sterics to be finely adjusted. Unfortunately, as far as cationic zirconium polymerization catalysts are concerned, the ligands do not seem stable enough to support a cationic zirconium center. We hypothesize that the instability of "cations" can be ascribed to the presence of Si, *either* "outside" the ligand backbone or "inside" the ligand backbone, rather than the presence of phosphorus per se. Therefore if olefin polymerization is the goal, we will have to prepare and test other types of diamidophosphine ligands that have no N−Si bonds. However, the diamido/phosphine ligands described here, in part because of their "hard/soft" multidentate nature, may offer opportunities for preparing a variety of complexes that contain a metal outside of group 4 in less demanding environments than in a zirconium "cation".

Experimental Section

General Details. All experiments were conducted under nitrogen in a Vacuum Atmospheres drybox, using standard Schlenk techniques, or on a high-vacuum line (<10^{-4} Torr). Pentane was washed with HNO$_3$/H$_2$SO$_4$ (5/95 v/v), sodium bicarbonate, and water, stored over CaCl$_2$, and then distilled from sodium benzophenone under nitrogen. Reagent grade benzene was distilled from sodium benzophenone under nitrogen. Toluene was distilled from molten sodium. Methylene chloride was distilled from CaH$_2$. Reagent grade ether and THF were sparged with nitrogen and passed through alumina columns.[50] Aldrich anhydrous grade DME was sparged with argon and brought into the drybox. All solvents were stored in the drybox over activated 4 Å molecular sieves. Deuterated solvents were freeze−pump−thaw degassed and vacuum transferred from an appropriate drying agent or sparged with argon and stored over 4 Å sieves. ^{1}H and ^{13}C data are listed in parts per million downfield from tetramethylsilane and were referenced using the residual protonated solvent peak. Unless otherwise noted, NMR experiments were run in C$_6$D$_6$ solution and ^{13}C and ^{31}P spectra were proton-decoupled. Coupling constants are given in hertz, and routine couplings are not listed. Elemental analyses (C, H, N) were performed on a Perkin-Elmer 2400 CHN analyzer in our own laboratory or by Kolbe Microanalytical Laboratory (Mülheim an der Ruhr, Germany). Column chromatography was performed by the method of Still.[51]

Zr(NMe$_2$)$_4$ was prepared by a literature procedure.[52] ClMe$_2$SiCH$_2$CH$_2$SiMe$_2$Cl was purchased from a commercial source. ^{13}CH$_3$MgI was prepared from ^{13}CH$_3$I (Cambridge Isotopes) and magnesium in ether. Grignard reagents were titrated with *n*-propanol using 1,10-phenanthroline as an indicator before use.

All X-ray data were collected on a Siemens SMART/CCD diffractometer with λ(Mo Kα) = 0.710 73 Å using ω scans and solved using a full-matrix least-squares refinement on F^2. No absorption correction was applied in any case. All procedures were analogous to those described elsewhere.[53] (See also the Supporting Information.)

ClCH$_2$CH$_2$(cyclo-NSiMe$_2$CH$_2$CH$_2$SiMe$_2$). A 1 L flask was charged with ClCH$_2$CH$_2$NH$_3$Cl (32.3 g, 0.278 mol), triethylamine (128 mL, 0.835 mol, 3.3 equiv), and 600 mL of CH$_2$Cl$_2$ (dried solvent is unnecessary). A solution of ClMe$_2$SiCH$_2$CH$_2$SiMe$_2$Cl in 200 mL of CH$_2$Cl$_2$ was prepared in the drybox. It was added slowly via a dropping funnel to the well-stirred slurry of ClCH$_2$CH$_2$NH$_3$Cl over a period of 1 h. The reaction mixture was stirred overnight, and the voluminous precipitate of NEt$_3$HCl was filtered off. The dichloromethane solution was evaporated, and the residue was extracted with hexane. The

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(53) Rosenberger, C.; Schrock, R. R.; Davis, W. M. *Inorg. Chem.* **1997**, *36*, 123.

NEt_3HCl was also thoroughly extracted with hexane. The extracts were combined, and the solvents were removed in vacuo. The residue was distilled in vacuo (bp 45 °C at 100 mTorr) to give the product as a colorless liquid, which became slightly cloudy upon standing; yield 45.3 g (73%): ^{1}H NMR δ 3.18 (m, 2, CH_2), 3.00 (m, 2, CH_2), 0.665 (s, 4, $SiCH_2CH_2Si$), 0.040 (s, 12, Me_2Si); ^{13}C NMR δ 45.6 (CH_2), 45.1 (CH_2), 8.12 ($SiCH_2CH_2Si$), −0.158 ($SiMe_2$).

PhP[CH_2CH_2(cyclo-$NSiMe_2CH_2CH_2SiMe_2$)]$_2$. In the drybox, a 500 mL Schlenk flask was charged with 300 mL of THF, $ClCH_2CH_2$(cyclo-$NSiMe_2CH_2CH_2SiMe_2$) (50.0 g, 0.225 mol), and a stir bar. It was fitted with a septum and connected to a Schlenk line. Phenylphosphine (12.4 mL, 0.113 mol) was introduced via syringe. The flask was cooled to −10 °C (ice/acetone bath) and fitted with an addition funnel containing 2.5 M LiBu in hexane (90.1 mL, 0.225 mol). The butyllithium solution was added dropwise over 1.5 h. After the addition was complete, the reaction was warmed to room temperature and stirred overnight. ^{31}P NMR showed clean conversion to product, which is stable enough to be worked up in air. The volatile components were removed in vacuo, and the residue was extracted with hexane (200 mL). This solution was filtered through a bed of Celite. The hexane was removed in vacuo to yield the product as a light yellow oil; yield 54.3 g (100%): ^{1}H NMR δ 7.50 (t, 2, Ph), 7.36 (d, 3, Ph), 2.81 (m, 4, CH_2), 1.80 (m, 4, CH_2), 0.655 (s, 8, $SiCH_2CH_2Si$), −0.0153 (s, 24, $SiMe_2$); ^{13}C NMR δ 139.1 (d, C_{ipso}), 132.7 (d, C_m), 129.1 (C_p), 128.7 (d, C_o), 39.8 (d, $^1J_{CP}$ = 24, NCH_2CH_2P), 34.6 (d, $^2J_{CP}$ = 15, NCH_2CH_2P), 8.37 ($SiCH_2CH_2Si$), 0.19 ($Si(CH_3)_2$); ^{31}P NMR (THF) −33.2.

PhP($CH_2CH_2NH_3Cl$)$_2$. Under air, a 500 mL round-bottomed flask was charged with PhP[CH_2CH_2(cyclo-$NSiMe_2CH_2CH_2SiMe_2$)]$_2$ (54.3 g, 0.113 mol) and 350 mL of ether. The reaction flask was cooled on an ice bath, and a dilute solution of HCl (24 mL of 12 M HCl in 75 mL of water) was added to the ethereal solution over 5 min. After 24 h the ether and water layers were separated, and the aqueous layer was washed with ether (2 × 100 mL). The water was removed by rotary evaporation with a bath temperature of 60 °C to give the crude product as an off-white oily mass. Ethanol (800 mL, sparged with argon) was added, and the mixture was heated under argon in an 80 °C oil bath for 20 min with good stirring. White microcrystals formed, which were isolated on a Büchner funnel. A second crop was obtained by reducing the volume of the mother liquor to ∼250 mL, which resulted in more product oiling out. Heating this mixture as before led to formation of a second crop of microcrystals. The product was dried at 50 °C in vacuo to remove the last traces of ethanol; yield 19.9 g (65%): ^{1}H NMR (DMSO-d_6) δ 8.22 (6, NH_3^+), 7.55 (2, Ph), 7.41 (3, Ph), 2.78 (br m, 4, NCH_2CH_2P), 2.10 (t, 4, NCH_2CH_2P); ^{31}P NMR (DMSO-d_6) δ −29.6.

PhP(CH_2CH_2NHTMS)$_2$. In the drybox, a 500 mL round-bottomed flask was charged with PhP($CH_2CH_2NH_3Cl$)$_2$ (10.0 g, 37.2 mmol) and 300 mL of THF. The slurry was cooled to −40 °C, and LiBu (2.5 M in hexanes, 59.4 mL, 149 mmol) was slowly added via syringe in small portions. After stirring the mixture at room temperature for 2.5 h it was again cooled to −40 °C, and Me_3SiCl (9.9 mL, 78.0 mmol) was added via syringe. The mixture was stirred for 3 h at 22 °C, and all solvents were removed in vacuo. The oily residue was extracted with 180 mL of pentane, and the extract was filtered through a bed of Celite. The pentane was removed from the filtrate in vacuo to give the product as a brown oil in quantitative yield (12.6 g): ^{1}H NMR δ 7.58 (t, 2, Ph), 7.12 (m, 3, Ph), 2.82 (m, 4, NCH_2CH_2P), 1.79 (m, 4, NCH_2CH_2P), 0.3 (br s, 2, NH), 0.01 (s, 18, $Si(CH_3)_3$); ^{13}C NMR δ 139.0 (d, C_{ipso}), 132.7 (d, C_m), 129.0 (d, C_p), 128.8 (d, C_o), 39.7 (d, $^1J_{CP}$ = 24, NCH_2CH_2P), 34.6 (d, $^2J_{CP}$ = 15), 8.37 ($SiCH_2CH_2Si$), 0.191 ($Si(CH_3)_2$); ^{31}P NMR δ −35.7.

PhP($CH_2CH_2NLiTMS$)$_2$. A 100 mL round-bottomed flask was charged with PhP(CH_2CH_2NHTMS)$_2$ (4.00 g, 11.7 mmol) and 70 mL of pentane. The mixture was cooled to −40 °C, and LiBu (2.5 M in hexanes, 9.4 mL, 24 mmol) was added. The reaction was stirred at 22 °C for 50 min, and the volume reduced to ∼30 mL in vacuo. The reaction was cooled to −40 °C, and crystallization of the product allowed to proceed. The product was filtered off and rinsed quickly with cold pentane. A second crop was obtained similarly for a combined yield of 2.54 g (62%): ^{1}H NMR (THF-d_8) δ 7.45 (t, 2, Ph), 7.24 (m, 3, Ph), 3.23 (m, 4, NCH_2CH_2P), 1.91 (m, 4, NCH_2CH_2P), −0.068 (s, 18, $Si(CH_3)_3$); ^{13}C NMR δ 143.6, 132.1, 128.8, 128.1 (Ph), 46.2 (d, $^1J_{CP}$ = 16, NCH_2CH_2P), 36.4 (NCH_2CH_2P), 2.11 ($Si(CH_3)_3$); ^{31}P NMR (THF-d_8) δ −29.2.

[N_2P]ZrCl$_2$. H_2[N_2P] (2.00 g, 5.87 mmol) was dissolved in 60 mL of pentane. The solution was cooled to −40 °C, and $Zr(NMe_2)_4$ (1.57 g, 5.87 mmol) was added as a solid. The reaction was stirred overnight and filtered to remove a small amount of precipitate. The solvents were removed under reduced pressure to give [N_2P]Zr(NMe_2)$_2$ as an oil that could not be induced to crystallize: ^{1}H NMR δ 7.35 (tt, 2, Ph), 7.02 (d, 3, Ph), 3.5 (m, 2, NCH_2CH_2P), 3.2 (m, 2, NCH_2CH_2P), 3.13 (s, 6, NMe_2), 3.05 (s, 6, NMe_2), 1.99 (m, 2, NCH_2CH_2P), 1.68 (m, 2, NCH_2CH_2P), 0.30 (s, 18, $SiMe_3$); ^{31}P NMR δ −10.5.

[N_2P]Zr(NMe_2)$_2$ was dissolved in 40 mL of pentane, and Me_3SiCl (1.49 mL, 11.7 mmol) was added by syringe. The reaction was stirred vigorously for 10 min and then allowed to stand for 2 h. The off-white crystalline solid that formed was isolated on a frit and dried in vacuo, 2.36 g (80%). No further purification was necessary, although the complex may be recrystallized from a mixture of toluene and pentane: ^{1}H NMR δ 7.63 (t, 2, Ph), 7.13 (m, 3, Ph), 2.94 (br m, 2, NCH_2CH_2P), 2.73 (m, 2, NCH_2CH_2P), 1.91 (m, 4, NCH_2CH_2P), 0.37 (s, 18, $SiMe_3$); ^{13}C NMR δ 133.0, 130.1, 129.0, 125.6 (Ph), 50.0 (d, J_{CP} = 15, NCH_2CH_2P), 38.3 (d, J_{CP} = 20, NCH_2CH_2P), 1.30 ($Si(CH_3)_3$); ^{31}P NMR δ 1.94. Anal. Calcd for $C_{16}H_{31}N_2PSi_2ZrCl_2$: C, 38.38; H, 6.24; N, 5.59. Found: C, 38.53; H, 6.20; N, 5.52.

[N_2P]Zr(CH_3)(THF)Cl. [N_2P]$ZrCl_2$ (300 mg, 0.599 mmol) was dissolved in 20 mL of ether, and the solution was cooled to −40 °C in the drybox freezer. MeMgCl (3.0 M in THF, 100 μL, 0.300 mmol) was added via syringe over a period of 4 min. The solution was placed back in the freezer for 15 min, and then another portion of MeMgCl (100 μL, 0.300 mmol) was added. After 30 min the solvents were removed in vacuo, and the reside was extracted with 40 mL of pentane. The extract was filtered through Celite, and the solvent removed in vacuo. The residue was recrystallized from pentane at −40 °C to give the product as white crystals, yield 140 mg (42%): ^{1}H NMR δ 7.32 (m, 2, Ph), 7.02 (m, 3, Ph), 3.64 (m, 4, THF), 3.2 (m, 4, NCH_2CH_2P), 1.8 (m, 4, NCH_2CH_2P), 1.33 (m, 4, THF), 0.84 (d, $^2J_{HP}$ = 7, 3, Me), 0.42 (s, 18, $SiMe_3$); ^{31}P NMR δ −0.49. Anal. Calcd for $C_{21}H_{42}N_2PSi_2ClOZr$: C, 45.66; H, 7.66; N, 5.07. Found: C, 45.54; H, 7.85; N, 5.02.

[N_2P]Zr(CH_3)Cl. [N_2P]$ZrCl_2$ (350 mg, 0.699 mmol) was dissolved in 20 mL of ether, and the solution was cooled to −40 °C. $MgMe_2$ (0.82 M in ether, 426 μL, 0.350 mmol) was added by syringe, and the reaction was stirred for 1 h at room temperature. The ether was removed in vacuo, and the residue was extracted with 40 mL of pentane. The extract was filtered through Celite, and the volume of the filtrate was reduced to ∼20 mL in vacuo. After storing the solution at −40 °C for 15 h the granular product was collected; yield 223 mg in two crops (66%): ^{1}H NMR δ 7.3 (m, 2, Ph), 6.95 (m, 3, Ph), 3.25 (m, 4, NCH_2CH_2P), 1.8 (m, 4, NCH_2CH_2P), 0.9 (s, 3, CH_3), 0.40 (s, 18, $SiMe_3$); ^{31}P NMR δ −1.6. Several attempts to obtain analytical data for [N_2P]Zr(CH_3)Cl failed.

[N_2P]Zr(i-Bu)Cl. [N_2P]$ZrCl_2$ (200 mg, 0.399 mmol) was dissolved in 15 mL of ether, and the solution was cooled to −40 °C. i-BuMgCl (2.16 M in ether, 185 μL, 0.399 mmol) was added by syringe, and the reaction was stirred at room temperature for 2 h. Dioxane (41 μL, 0.479 mmol) was added, and the precipitate allowed to settle for 30 min. The mixture was filtered through a short plug of Celite, and the solvents were removed in vacuo. The residue was dissolved in ∼1 mL

of ether, to which a layer of pentane was carefully added. The product precipitated as a light yellow powder as the solvents slowly diffused together; yield 137 mg (66%): ^{1}H NMR δ 7.34 (m, 2, Ph), 7.03 (m, 3, Ph), 3.3 (dt, 4, NCH_2CH_2P), 2.1 (sept, 1, $CH_2CH(CH_3)_2$), 1.88 (m, 4, NCH_2CH_2P), 1.5 (virtual triplet, $^3J_{HP} = 7.7$, $^3J_{HH} = 6.8$, 2, $CH_2CH(CH_3)_2$), 1.07 (d, 6, $CH_2CH(CH_3)_2$), 0.37 (s, 18, $SiMe_3$); ^{13}C NMR δ 134, 132, 130, 129 (Ph), 70.9 ($CH_2CH(CH_3)_2$), 48 (d, NCH_2CH_2P), 37.8 (d, NCH_2CH_2P), 29.9 (d, $^3J_{CP} = 5$, $CH_2CH(CH_3)_2$), 28.2 (s, $CH_2CH(CH_3)_2$), 1.1 (s, $Si(CH_3)_3$; ^{31}P NMR δ 1.19. Anal. Calcd for $C_{20}H_{40}N_2Si_2PClZr$: C, 45.99; H, 7.72; N, 5.36. Found: C, 45.52; H, 7.53; N, 5.37.

[N$_2$P]Zr(CH$_3$)$_2$. [N_2P]$ZrCl_2$ (260 mg, 0.519 mmol) was dissolved in 15 mL of ether. The solution was cooled to −40 °C, and MeMgCl (3.0 M in THF, 346 μL, 1.04 mmol) was added by syringe. The reaction was stirred for 45 min at room temperature. The volatile components were removed in vacuo, and the residue was extracted with 12 mL of pentane. After 1 h the mixture was filtered and the solvents were removed from the filtrate in vacuo to yield the product as an oil (220 mg, 92%) that could not be induced to crystallize: ^{1}H NMR δ 7.3 (m, 2, Ph), 7.0 (m, 3, Ph), 3.4 (m, 2, NCH_2CH_2P), 3.1 (m, 2, NCH_2CH_2P), 1.8 (m, 2, NCH_2CH_2P), 1.62 (m, 2, NCH_2CH_2P), 0.80 (d, $^2J_{HP} = 6$, 3, *cis*-Me), 0.60 (s, 3, *trans*-Me).

[N_2P]Zr($^{13}CH_3$)$_2$ was prepared similarly: ^{13}C NMR δ 35.9 ($^2J_{CP} = 29$, $^1J_{CH} = 113$), 40.9 ($^2J_{CP} = 2$, $^1J_{CH} = 114$); ^{31}P NMR δ −15.7.

[N$_2$P]Zr(CH$_2$Ph)$_2$. [N_2P]$ZrCl_2$ (150 mg, 0.300 mmol) was dissolved in 10 mL of ether. The solution was cooled to −40 °C, and $C_6H_5CH_2MgCl$ (1.0 M in ether, 599 μL, 0.599 mmol) was added by syringe. After 3 h, a ^{31}P NMR spectrum showed that the reaction was complete. Dioxane (56 μL, 0.66 mmol) was added, and the precipitate was allowed to settle. The reaction was filtered through Celite, and the volatile components were removed under reduced pressure. The residue was recrystallized from a mixture of ether and pentane at −40 °C to give the product as yellow crystals (120 mg in two crops; 65%): ^{1}H NMR δ 7.28 (d, 4, Ph), 7.05 (m, 2, Ph), 6.95 (m, 2, Ph), 6.7 (m, 2, Ph), 3.15 (m, 2, NCH_2CH_2P), 2.8 (m, 2, NCH_2CH_2P), 2.75 (d, $^3J_{HP} = 6.6$, 2, *cis*-$CH_2C_6H_5$), 2.69 (d, $^3J_{HP} = 2.4$, 2, *trans*-$CH_2C_6H_5$), 1.65 (m, 4, NCH_2CH_2P), 0.294 (s, 18, $SiMe_3$); ^{13}C NMR δ 149.6 (C_{ipso}), 143.5 (C_m), 135.9 (C_p), 131.7 (C_o), 129.3, 128.9, 128.8, 128.7, 127.3, 126.8, 122.3, 120.8, 69.3 ($^2J_{CP} = 3.2$, $^1J_{CH} = 126$, *cis*-$CH_2C_6H_5$), 65.9 ($^2J_{CP} = 22$, $^1J_{CH} = 118$, *trans*-$CH_2C_6H_5$), 47.7 (d, NCH_2CH_2P), 37.1 (d, NCH_2CH_2P), 1.40 ($SiMe_3$); ^{31}P NMR δ −7.08. Anal. Calcd for $C_{30}H_{45}N_2PSi_2Zr$: C, 58.87; H, 7.41; N, 4.58. Found: C, 58.71; H, 7.55; N, 4.47.

[N$_2$P]Zr(^{13}CH$_3$)(CH$_2$Ph). [N_2P]$ZrCl_2$ (250 mg, 0.499 mmol) was dissolved in 20 mL ether, and the solution was cooled to −40 °C. $^{13}CH_3MgI$ (1.4 M in ether, 423 μL, 0.50 mmol) was added by syringe, and the reaction was stirred for 40 min. The reaction mixture was again cooled to −40 °C, and $C_6H_5CH_2MgCl$ (1.0 M in ether, 500 μL, 0.499 mmol) was added. The mixture was stirred for 1.3 h, and dioxane (98 μL) was added. The precipitate was allowed to settle for 45 min, and the solution was filtered through a plug of Celite. The ether was removed from the filtrate in vacuo, and the crude product was recrystallized from ether, 169 mg (63%): ^{1}H NMR δ 7.4 (t, Ph), 7.1 (m, Ph), 6.8 (t, Ph), 3.25 (m, 2, NCH_2CH_2P), 2.82 (d, $^3J_{HP} = 9$, *cis*-$CH_2C_6H_5$), 2.61 (m, 2, NCH_2CH_2P), 1.8 (m, 2, NCH_2CH_2P), 1.62 (m, NCH_2CH_2P), 0.588 (d, 3, *trans*-^{13}Me), 0.304 (s, 18, $SiMe_3$); ^{13}C NMR δ 131.9, 129,7 128.9, 127.4, 122.3, 62.4 (*cis*-$CH_2C_6H_5$, $^2J_{CP} = 4.6$, $^1J_{CH} = 130$), 48.7 (NCH_2CH_2P), 38.2 (d, *trans*-$^{13}CH_3$, $^2J_{CP} = 27.9$), 37.7 (NCH_2CH_2P), 0.927 ($SiMe_3$); ^{31}P NMR δ −6.56 (d). Anal. Calcd for $C_{24}H_{41}N_2PSi_2Zr$ (all natural abundance ^{13}C): C, 53.78; H, 7.71; N, 5.23. Found: C, 54.08; H, 7.32; N, 5.17.

ClCH$_2$SiMe$_2$NH(t-Bu). A solution of dry t-BuNH_2 (53.7 g, 0.73 mol) in diethyl ether (300 mL) was cooled to −35 °C in the drybox. A solution of $ClCH_2SiMe_2Cl$ (50 g, 0.35 mol) was added, and a white precipitate formed. The reaction mixture was stirred overnight at room temperature, and the solvents were removed in vacuo. The residue was extracted with pentane. The extract was filtered through Celite, and the pentane was removed from the filtrate in vacuo to give a colorless oil (59 g, 0.33mol; 94% yield). ^{1}H NMR δ 2.57 (s, 2, CH_2), 0.99 (s, 9, t-Bu), 0.5 (br s, 1, NH), 0.11 (s, 6, $Si(CH_3)$; $^{13}C\{^1H\}$ δ 49.7 (s, $NC(CH_3)_3$), 34.0 (s, $NC(CH_3)_3$), 32.4 (s, NCH_2-Si), 0.7 (s, $Si(CH_3)_2$).

PhP(CH$_2$SiMe$_2$NH-t-Bu)$_2$. A solution of 2.5 M LiBu in hexane (58.5 mL, 1.5 mol) and a solution of $PhPH_2$ (15.4 g, 1.4 mol) in diethyl ether (300 mL) were cooled to −35 °C in the drybox. The LiBu solution was then added to the phosphine solution. The mixture stood for 1 h at room temperature. A solution of $ClCH_2SiMe_2NH$-t-Bu (25.2 g, 1.4 mol) in diethyl ether (30 mL) was then added at −35 °C, and the reaction mixture was stirred for 1 h at room temperature. Again the reaction mixture was cooled to −35 °C, and another 58 mL of 2.5 M LiBu solution was added. The mixture stood for 1 h at room temperature, and a solution of $ClCH_2SiMe_2NH$-t-Bu (25.2 g, 1.4 mol) in diethyl ether was then added at −35 °C. The reaction mixture was stirred for 2 h at room temperature, and the solvent was removed in vacuo. The residue was extracted with pentane, and the extract was filtered through Celite. The solvent was removed from the filtrate in vacuo to afford a pale yellow oil that was distilled (105 °C, 100 mTorr) to give the product as a colorless oil (47 g, 1.19 mol; 85% yield): ^{1}H NMR δ 7.68 (m, 2, Ph), 7.18 (m, 3, Ph), 1.14 (m, 2, CH_aH_b), 1.08 (s, 18, t-Bu), 0.99 (m, 2, CH_aH_b), 0.55 (br s, 2, NH), 0.17 (s, 6, SiMe), 0.15 (s, 6, SiMe); $^{13}C\{^1H\}$ δ 133.7 (d, $^1J_{CP} = 22$, C_{ipso}), 129.6 (C_m), 128.9 (C_p), 128.7 (C_o), 49.9 ($NC(CH_3)_3$), 34.2 ($NC(CH_3)_3$), 22.9 (d, $^1J_{CP} = 30$, CH_2), 3.6 (d, $^3J_{CP} = 4$, $Si(CH_3)_a(CH_3)_b$), 3.5 (d, $^3J_{CP} = 4$, $Si(CH_3)_a(CH_3)_b$); $^{31}P\{^1H\}$ δ −34.4. Anal. Calcd for $C_{20}H_{41}N_2PSi_2$: C, 60.55; H, 10.42; N, 7.06. Found: C, 60.57; H, 10.34; N, 7.12.

[t-Bu$_2$NPN]ZrCl$_2$. A −35 °C solution of $PhP[CH_2SiMe_2N(Li)(t\text{-Bu})]_2$ (2.88 g, 7 mmol) in diethyl ether (15 mL) was added to a slurry of $ZrCl_4(THF)_2$ (2.66 g, 7 mmol) in diethyl ether (40 mL) at −35 °C, and the reaction was stirred overnight at room temperature. The reaction mixture was filtered through Celite, and the volume of the filtrate was reduced to 15 mL in vacuo. The product crystallized upon storing the solution overnight at −35 °C; yield 2.5 g (4.5 mmol, 64%): ^{1}H NMR δ 7.95 (m, 2, Ph), 7.11 (m, 3, Ph), 1.59 (s, 18, t-Bu), 1.27 (br m, 2, CH_aH_b), 0.82 (m, 2, CH_aH_b), 0.24 (s, 6, SiMe), 0.15 (br s, 6, SiMe); $^{13}C\{^1H\}$ δ 134.0 (d, $^1J_{CP} = 10$, C_{ipso}), 131.3 (C_m), 129.3 (C_p), 129.2 (C_o), 60.0 ($NC(CH_3)_3$), 33.6 ($NC(CH_3)_3$), 17.9 (CH_2), 7.1 ($Si(CH_3)_a(CH_3)_b$), 5.9 (d, $^3J_{CP} = 8$, $Si(CH_3)_a(CH_3)_b$); $^{31}P\{^1H\}$ (C_6D_6) δ −10.9; $^{31}P\{^1H\}$ (THF) δ −9.8.

The compound was also recrystallized from C_6H_6 by dissolving it in hot C_6H_6 and cooling the solution to room temperature overnight. Large colorless crystals were collected whose proton NMR spectrum in toluene showed 5/6 molecule of C_6H_6 per Zr atom to be present. Anal. Calcd for $C_{25}H_{44}Cl_2N_2PSi_2Zr$: C, 48.28; H, 7.13; N, 4.50. Found: C, 48.20; H, 7.13; N, 4.51.

[t-Bu$_2$NPN]ZrMeCl. A 1.4 M solution of LiMe (256 mL, 0.36 mmol) in diethyl ether was added to a solution of $[PhP(CH_2SiMe_2N\text{-}t\text{-}Bu)_2]ZrCl_2$ (200 mg, 0.36 mmol) in diethyl ether (6 mL). The reaction was stirred at room temperature for only 5 min before filtering the cloudy yellow solution through glasswool paper. The yellow filtrate was placed in the −30 °C freezer overnight, and white crystals were isolated (120 mg, 0.225 mmol; 62%): ^{1}H NMR (CD_2Cl_2) δ 7.78 (m, 2, Ph), 7.43 (m, 3, Ph), 1.63 (s, 18, t-Bu), 1.59 (m, 2, CH_aH_b), 1.21 (m, 2, CH_aH_b), 0.58 (d, $^3J_{HP} = 11$, 3, ZrMe), 0.41(br s, 6, SiMe), 0.18 (br s, 6, SiMe); $^{31}P\{^1H\}$ (CD_2Cl_2) δ −0.5. Anal. Calcd for $C_{21}H_{42}ClN_2PSi_2Zr$: C, 47.02; H, 7.89; N, 5.22. Found: C, 46.88; H, 7.95; N, 5.09.

{[t-BuNSiMe$_2$CH$_2$P(Ph)CH$_2$SiMe$_2$N]ZrMe}$_2$. A −35 °C 1.4 M solution of LiMe (512 μL, 0.72 mmol) in diethyl ether

was added to a solution of [t-Bu_2NPN]$ZrCl_2$ (200 mg, 0.36 mmol) in diethyl ether (8 mL). The reaction was stirred at room temperature for 10 min. A white precipitate formed, and the reaction mixture turned pale yellow. The solvents were removed in vacuo, and the residue was extracted with 8 mL of pentane. The extract was filtered, and the volume was reduced to ~1 mL in vacuo. The product is highly soluble in pentane, but 40 mg (0.09 mmol, 25%) could be isolated in crystalline form upon storing a pentane solution at −35 °C for several days: ^{1}H NMR δ 7.78 (m, 2, Ph), 7.18 (m, 3, Ph), 1.64 (s, 9, t-Bu), 1.32 (m, 2, C$H_a$$H_b$), 0.98 (m, 2, C$H_a$$H_b$), 0.87 (d, $^3J_{HP}$ = 10, 3, ZrMe), 0.68 (s, 3, SiMe), 0.60 (s, 3, SiMe), 0.34 (s, 3, SiMe), −0.07 (s, 3, SiMe); ^{31}P{^{1}H} δ -19.8.

ClCH$_2$SiMe$_2$NHAr. Li[NH(2,6-$Me_2C_6H_3$)] (16.1 g, 127 mmol) was added as a solid to a solution of $ClCH_2SiMe_2Cl$ (18.2 g, 127 mmol) in diethyl ether (120 mL) at −35 °C. A white solid formed, and the reaction was stirred overnight at room temperature. The mixture was then filtered through Celite, and solvents were removed from the filtrate in vacuo to give a yellow oil (26 g, 114 mmol, 90%); this crude material was distilled (200 mTorr; 90 °C) to afford a colorless oil (23.9 g, 105 mmol): ^{1}H NMR δ 6.95 (m, 2, H_m), 6.84 (m, 1, H_p) 2.53 (s, 2, CH_2), 2.08 (s, 6, Me_o), 0.04 (s, 6, SiMe).

PhP(CH$_2$SiMe$_2$NHAr)$_2$. Phenylphosphine (4.9 g, 45 mmol) and $ClCH_2SiMe_2NH$(2,6-$Me_2C_6H_3$) (20.3 g, 90 mmol) were dissolved in diethyl ether (120 mL), and the solution was cooled to −35 °C. A 2.5 M solution of LiBu in hexane (35.6 mL, 90 mmol) was then added at −35 °C. A white precipitate of LiCl formed immediately. The reaction was stirred overnight at room temperature, and the solvents were removed in vacuo. The residue was extracted with pentane (2 × 100 mL), and LiCl was filtered off through Celite. The solvent was removed from the filtrate in vacuo to give the product as a pale yellow oil in quantitative yield: ^{1}H NMR δ 7.58 (m, 2, PhP), 7.05 (m, 3, PhP), 6.96 (m, 2, H_m), 6.85 (m, 1, H_p), 2.08 (s, 6, Me_o), 1.06 (m, 2, CH_2), 0.04 (s, 6, SiMe), 0.01 (s, 6, SiMe); ^{13}C{^{1}H} δ 144.0, 133.5 (d, $^1J_{CP}$ = 25), 132.1, 129.9, 129.08, 129.04, 128.96, 122.5, 22.0 (d, $^1J_{CP}$ =19, CH_2), 20.5 (s, ArMe), 1.6 (d, $^3J_{CP}$ = 4.5, SiMe), 1.5 (d, $^3J_{CP}$ = 4, SiMe); ^{31}P{^{1}H} δ −36.1. Anal. Calcd for $C_{28}H_{41}N_2PSi_2$: C, 68.25; H, 8.39; N, 5.68. Found: C, 68.12; H, 8.44; N, 5.74.

[Ar$_2$NPN]Zr(NMe$_2$)$_2$. H_2[Ar_2NPN] (3.6 g, 7.3 mmol) was dissolved in 50 mL of pentane, and $Zr(NMe_2)_4$ (2.0 g, 7.3 mmol) was added as a solid at room temperature. The reaction was stirred overnight and filtered to remove a small amount of precipitate. The solvents were removed under reduced pressure to give [Ar_2NPN]$Zr(NMe_2)_2$ as a white solid in quantitative yield. An analytically pure sample was obtained by recrystallization from pentane at −35 °C: ^{1}H NMR δ 7.63 (m, 2, PhP), 7.20 (m, 3, PhP), 7.06 (d, 4, H_m), 6.79 (t, 2, H_p), 3.08 (s, 6, NMe_2), 2.39 (s, 6, Me_o), 2.38 (s, 6, Me_o), 1.97 (s, 6, NMe_2), 1.26 (m, 4, $SiCH_2P$), 0.18 (s, 6, SiMe), −0.08 (s, 6, SiMe); ^{31}P NMR δ −27.9. Anal. Calcd for $C_{32}H_{51}N_4PSi_2Zr$: C, 57.35; H, 7.67; N, 8.36. Found: C, 57.06; H, 7.45; N, 8.18.

[Ar$_2$NPN]ZrCl$_2$. [Ar_2NPN]$Zr(NMe_2)_2$ (1.64 g, 2.45 mmol) was dissolved in 50 mL of ether, and a 1.0 M solution of HCl in ether (4.9 mL, 4.9 mmol) was added by syringe at −35 °C. The reaction was stirred vigorously for 2 h. The solution was concentrated to 30 mL and was allowed to stand overnight. The white crystalline solid that formed was isolated on a frit and dried in vacuo, 1.35 g (84%): ^{1}H NMR δ 7.96 (m, 2, PhP), 7.15 (m, 3, PhP), 7.00 (d, 4, H_m), 6.90 (t, 2, H_p), 2.50 (s, 12, Me_o), 1.24 (m, 4, CH_2), 0.16 (s, 6, SiMe), −0.20 (s, 6, SiMe); ^{13}C{^{1}H} (60 °C) δ 147.07, 147.02, 136.3, 136.1, 135.1 (d, $^1J_{CP}$ = 16), 132.7, 132.6, 131.1, 129.9, 129.5, 129.4, 125.9, 22.0 (s, Me_o), 21.6 (s, Me_o), 18.8 (d, $^1J_{CP}$ = 5, CH_2), 3.8 (d, $^3J_{CP}$ = 4.6, SiMe), 2.0 (d, $^3J_{CP}$ = 3.8, SiMe); ^{31}P{^{1}H} δ −15.2. Anal. Calcd for $C_{28}H_{39}Cl_2N_2PSi_2Zr$: C, 51.51; H, 6.02; N, 4.29; Cl, 10.86. Found: C, 51.38; H, 6.05; N, 4.22; Cl, 10.95.

[Ar$_2$NPN]ZrMeCl. A 3.0 M solution of MeMgBr in ether (150 μL, 0.46 mmol) was added to a solution of [Ar_2NPN]$ZrCl_2$ (300 mg, 0.46 mmol) in CH_2Cl_2 (8 mL) at −35 °C. The reaction mixture was stirred at room temperature for 1 h. The solution was treated with dioxane, and the cloudy mixture was filtered. The solvents were removed from the filtrate in vacuo and the off-white crystalline material was recrystallized from dichloromethane/pentane mixtures to give X-ray crystallography quality crystals in 30% yield (87 mg, 0.14 mmol): ^{1}H NMR (CD_2Cl_2) δ 7.74 (m, 2, PhP), 7.51 (m, 3, PhP), 7.05 (m, 4, H_m), 7.02 (m, 2, H_p), 2.40 (s, 6, Me_o), 2.22 (s, 6, Me_o), 1.73 (m, 4, CH_2), 0.54 (d, $^3J_{HP}$ = 8.8, 3, ZrMe), 0.28 (s, 6, SiMe), 0.04 (s, 6, SiMe); ^{31}P{^{1}H} (CD_2Cl_2) δ −12.0.

[Ar$_2$NPN]ZrMe$_2$. A 3.0 M solution of MeMgBr in ether (306 μL, 0.92 mmol) was added to a stirred slurry of [Ar_2NPN]$ZrCl_2$ (300 mg, 0.46 mmol) in diethyl ether (8 mL) at −35 °C. The reaction mixture was stirred at room temperature for 1 h. Dioxane was added, and the reaction mixture was stirred for an additional 20 min. The resulting milky solution was filtered through Celite. The solvents were removed from the filtrate in vacuo, and the white crystalline material was freeze-dried using 4 mL of benzene. The product was obtained in quantitative yield as a white powder (276 mg, 0.45 mmol). No further purification was necessary, although the complex may be recrystallized from dichloromethane/pentane mixtures to afford large colorless crystals in 47% yield: ^{1}H NMR δ 7.70 (m, 2, H_p), 7.2−6.9 (m, 4, aryl), 2.38 (s, 3, Me_o), 2.26 (s, 3, Me_o), 1.21 (m, 4, CH_2), 0.88 (d, $^3J_{HP}$ = 6.6, 3, Me_{eq}), 0.16 (s, 6, SiMe), −0.05 (s, 6, SiMe), −0.24 (d, $^3J_{HP}$ = 1.5, 3, Me_{ax}); ^{13}C{^{1}H} δ 144.1, 143.9, 138.9, 138.8, 136.6 (d, $^1J_{CP}$ = 16), 132.5, 132.3, 130.3, 129.9, 129.6, 129.4, 129.3, 125.1, 46.4 (d, $^2J_{CP}$ = 30.1, Me_{ax}), 45.0 (d, $^2J_{CP}$ = 6.2, Me_{eq}), 22.0 (s, Me_o), 21.4 (s, Me_o), 18.5 (d, $^1J_{CP}$ = 13, CH_2), 3.7 (d, $^3J_{CP}$ = 5.0, SiMe), 2.9 (d, $^3J_{CP}$ = 3.5, SiMe); ^{31}P{^{1}H} δ −23.7. Anal. Calcd for $C_{30}H_{45}N_2PSi_2Zr$: C, 58.87; H, 7.41; N, 4.58. Found: C, 58.78; H, 7.29; N, 4.58.

[Ar_2NPN]Zr($^{13}CH_3$)$_2$ was prepared similarly: ^{13}C NMR δ 46.0 ($^2J_{CP}$ = 31, $^1J_{CH}$ = 113), 45.1 ($^2J_{CP}$ = 6.2, $^1J_{CH}$ = 115).

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Supporting Information Available: Tables giving crystal data and structure refinement details, atomic coordinates, bond lengths and angles, and anisotropic displacement parameters for [N_2P]$Zr(CH_3)(CH_2Ph)$, [t-Bu_2NPN]ZrMeCl, [Ar_2-NPN]ZrMeCl, and {[t-BuNSi$Me_2$$CH_2$P(Ph)$CH_2SiMe_2$N]ZrMe}$_2$ (24 pages). Ordering information is given on any current masthead page.

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