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Synthesis of the Amidoimido Zirconium Anion $[(HNtBu)(NtBu)Zr\{(PNtBu)_2(NtBu)_2\}]^-$ under Reductive Conditions[†]

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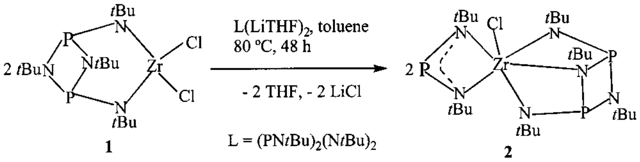
*Summary: Reaction of (η^2-L)$ZrCl_2$ (**1**, L = $(PNtBu)_2(NtBu)_2$) with 0.5 equiv of L$(Li{\cdot}THF)_2$ in toluene results in the cleavage of the lithiated bis(tert-butylamido)cyclodiphosph(III)azane and the formation of the zirconium compound (η^3-L)[η^2-$(NtBu)_2P$]ZrCl (**2**). Treatment of **2** with K/Na alloy leads to the cleavage of two P−N bonds of the η^2-$(NtBu)_2P$ ligand and the formation of the amidoimido zirconium complex [{(HNtBu)(NtBu)Zr(η^3-L)}$^-${K(η^6-C_7H_8)}$^+$] (**3**).*

Introduction

Group 4 imido complexes have attracted considerable attention since the discovery of C−H bond activation by zirconium imido compounds in 1988.[1] A variety of group 4 imido complexes supported by different ligands has been successfully prepared,[2] and significant progress has been achieved using these compounds.[3]

We are interested in studying the derivatives with amido, imido, and nitrido groups formed during the reactions of early transition metal precursors with nitrogen-containing compounds. The first terminal titanium imido complex, $Ph_2P(S)N{=}TiCl_2{\cdot}3C_5H_5N$, was structurally characterized by us in 1990.[4] Moreover, we reported already on the preparation of a series of group 4 metal imido bridged dinuclear complexes[5] and the monomers with terminal imido ligands.[6] More recently, the first unsubstituted imido (NH) bridged dinuclear zirconium compound $[(\eta^3\text{-L})Zr(\mu\text{-NH})]_2$ (L = $(PNtBu)_2(NtBu)_2$) has been prepared in the presence of KH in a liquid ammonia/toluene two-phase system.[7] Herein, we describe the synthesis of the amido zirconium chloride (η^3-L)[η^2-$(NtBu)_2P$]ZrCl (**2**) and the amidoimido zirconium complex [{(HN*t*Bu)(N*t*Bu)Zr(η^3-L)}$^-${K(η^6-C_7H_8)}$^+$] (**3**).

Scheme 1



1 **2**

Results and Discussion

Treatment of (η^2-L)$ZrCl_2$ (**1**)[7] with 0.5 equiv of L$(Li{\cdot}THF)_2$ in toluene at 80 °C leads to the yellow crystals of the amido zirconium chloride (η^3-L)[η^2-$(NtBu)_2P$]ZrCl (**2**; Scheme 1) in 58% yield. During this reaction, the nucleophilic L^{2-} is cleaved to give two $(NtBu)_2P$ ligands. The mechanism is not clear; the zirconium compound **1** seems crucial for this cleavage. Further reaction of **2** with 2 equiv of K/Na alloy in toluene yields the amidoimido zirconium potassium complex [{(HN*t*Bu)(N*t*Bu)Zr(η^3-L)}$^-${K(η^6-C_7H_8)}$^+$] (**3**; Scheme 2). In the latter reaction the cleavage of the two P−N bonds of the η^2-$(NtBu)_2P$ ligand by alkali metals results in the formation of a compound containing a Zr=N double bond. Although we have little information how the (HN*t*Bu) ligand is formed, it is most likely that the proton of the amido ligand is introduced by the C−H bond activation

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[†] Dedicated to Professor Neil Bartlett on the occasion of his 70th birthday.

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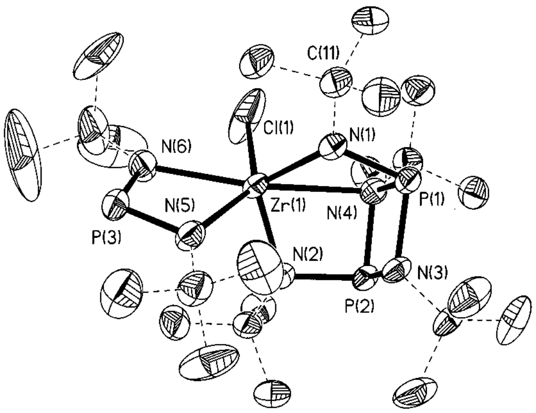
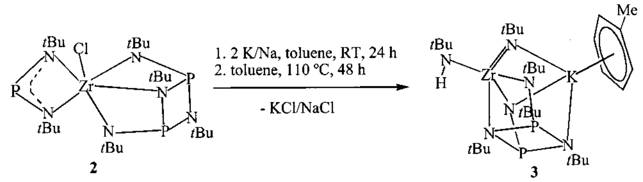


Figure 1. Molecular structure of **2** (50% probability ellipsoids).

Scheme 2



of the ligand or the solvent by zirconium compounds and alkali metals (reduction of Cp_2ZrRCl ($Cp = C_5H_5$; $R = n$-octyl) by Na/Hg in THF gives high yields of RH[8]). Obviously, the bulky ligands on zirconium are essential for stabilizing the imido zirconium monomer **3**.

Compounds **2** and **3** are yellow crystalline solids. **2** is stable above the melting point (267 °C), while **3** starts to decompose at 290 °C. The IR spectrum of **3** shows a broad absorption at 3373 cm^{-1}, assignable to the N−H stretching frequency. The resonance of the NH proton in the ^1H NMR spectrum of **3** appears as a broad singlet (δ 4.58 ppm). The most intense peak in the EI mass spectrum of **2** appears at *m/e* 471 ($M^+ - (NtBu)_2P$), and the signal at 644 (18%) is assigned to the molecular ion. Compound **3** exhibits the fragments ($M^+ - C_7H_8$) and (K^+) at 618 (3%) and 39 (100%), respectively.

The molecular structures of **2** and **3** are shown in Figures 1 and 2. Details of the data collection, structure solution, and refinement are given in Table 1.

Compounds **2** and **3** crystallize in the triclinic and orthorhombic space group $P\bar{1}$ and $P2(1)2(1)2(1)$, respectively. The molecular structure of **2** in the crystal shows that one η^3-L ligand, one η^2-$(NtBu)_2P$ group, and one chlorine atom complete the coordination sphere of Zr. The bond lengths Zr(1)−N(1) (2.091(2) Å), Zr(1)−N(2) (2.099(2) Å), and Zr(1)−N(4) (2.568(2) Å) are comparable to those found in $[(\eta^3\text{-L})Zr(\mu\text{-NH})]_2$ (2.116(7), 2.129(7), and 2.399(7) Å)[7] and in $[(MeSiNtBu)_2(NtBu)_2]ZrCl_2$ (2.075(3), 2.089(3), and 2.523(3) Å).[9] The sum of the angles at N(1) and N(2) is 357.5° and 359.0°, respectively. The approximately trigonal planar coordination indicates that the N(1) and N(2) atoms are nearly sp^2 hybridized; the N(1) and N(2) atoms donate their lone-pair electrons into the empty d-orbitals of zirconium as three-electron donors in analogy with the bonding situation in $[(\eta^3\text{-L})Zr(\mu\text{-NH})]_2$ and $[(MeSiNtBu)_2(NtBu)_2]ZrCl_2$. A planar four-membered P(1)N(3)P(2)N(4) ring of the η^3-L ligand (the sum of the angles within the ring is 359.9°) is found in **2**. The bond lengths P(1)−N(1) (1.698(2) Å), P(1)−N(3) (1.744(2) Å), and P(1)−N(4) (1.777(2) Å) are similar to those found in $[(\eta^3\text{-L})Zr(\mu\text{-NH})]_2$ (1.686(8), 1.733(8), and 1.789(8) Å)[7] and in $[(\eta^3\text{-L})In]_2$ (1.670(3), 1.723(3), and 1.801(3) Å).[10]

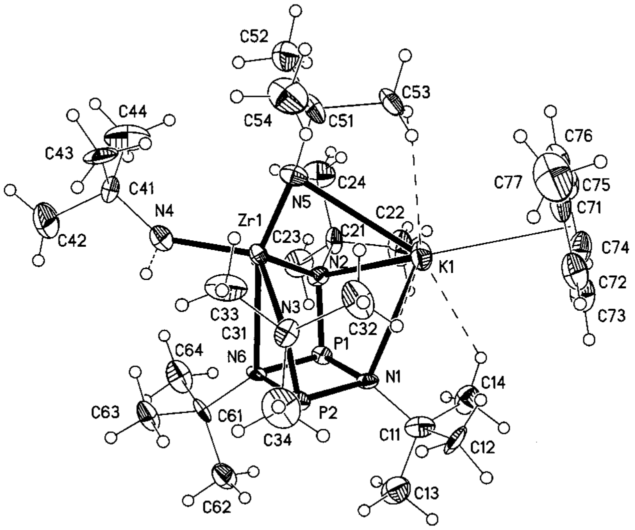


Figure 2. Molecular structure of **3** (50% probability ellipsoids).

Table 1. Crystallographic Data for 2 and 3

	2	3
empirical formula	$C_{24}H_{54}ClN_6P_3Zr$	$C_{24}H_{55}KN_6P_2Zr{\cdot}C_7H_8$
fw	646.33	620.02 + 92.14
cryst size (mm)	0.3 × 0.3 × 0.3	1.0 × 1.0 × 0.8
cryst syst	triclinic	orthorhombic
space group	$P\bar{1}$	$P2(1)2(1)2(1)$
a (Å)	10.133(2)	11.893(2)
b (Å)	11.660(2)	13.141(3)
c (Å)	14.297(3)	24.840(5)
α (deg)	91.47(3)	90
β (deg)	98.83(3)	90
γ (deg)	91.17(3)	90
cell volume V ($Å^3$)	1668.2(6)	3882.0(13)
Z	2	4
ρ_c (g mm^{-3})	1.287	1.218
μ (mm^{-1})	0.576	0.500
$F(000)$	684	1520
2θ range (deg)	7.38−51.18	7.02−50.08
no. of data: measd, unique	7312, 6228 ($R_{int} = 0.0903$)	5286, 4796 ($R_{int} = 0.0903$)
R,[a] wR_2[b] ($I > 2\sigma(I)$)	0.0414, 0.1119	0.0917, 0.2593
R, wR_2 (all data)	0.0428, 0.1138	0.1008, 0.2698
goodness of fit, S[c]	1.054	1.110
no. of refiend params	334	389
no. of restraints	0	0
largest diff peak, hole (e $Å^{-3}$)	+1.193/−1.301	+2.722/−1.724

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR_2 = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)]^{1/2}$. [c] $S = [\sum w(F_o^2 - F_c^2)^2/\sum(n - p)]^{1/2}$.

The P(3)−N(5) (1.599(2) Å) and P(3)−N(6) (1.610(2) Å) bond lengths are shorter than those of the P−N bonds found in aminophosphines $R_2N{-}PR_2$ (ranging from ca. 1.62 to 1.78 Å)[11] and longer than those of the P=N double bonds found in RN=PR (ca. 1.55 Å),[12] which are

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Table 2. Selected Bond Lengths (Å) and Bond Angles (deg) for (η^3-L)[η^2-(N*t*Bu)$_2$P]ZrCl (2)

Bond Lengths			
Zr(1)−N(1)	2.091(2)	Zr(1)−N(2)	2.099(2)
Zr(1)−N(4)	2.568(2)	Zr(1)−N(5)	2.289(2)
Zr(1)−N(6)	2.270(2)	Zr(1)−Cl(1)	2.456(3)
Zr(1)−Cl(1′)	2.479(1)	P(1)−N(1)	1.698(2)
P(1)−N(3)	1.744(2)	P(1)−N(4)	1.777(2)
P(1)−P(2)	2.646(1)	P(3)−N(5)	1.599(2)
P(3)−N(6)	1.610(2)		
Bond Angles			
N(3)−P(1)−N(4)	82.34(9)	N(3)−P(2)−N(4)	82.47(9)
P(1)−N(3)−P(2)	98.5(1)	P(2)−N(4)−P(1)	96.6(1)
C(11)−N(1)−P(1)	119.2(2)	C(11)−N(1)−Zr(1)	132.3(2)
P(1)−N(1)−Zr(1)	106.0(1)	C(21)−N(2)−Zr(1)	136.6(2)
P(2)−N(2)−Zr(1)	105.4(1)	C(21)−N(2)−P(2)	117.0(2)
N(5)−P(3)−N(6)	98.6(1)	C(51)−N(5)−P(3)	120.3(2)
C(51)−N(5)−Zr(1)	141.5(2)	P(3)−N(5)−Zr(1)	98.2(1)
C(61)−N(6)−P(3)	119.3(2)	C(61)−N(6)−Zr(1)	142.0(2)
P(3)−N(6)−Zr(1)	98.6(1)		

Table 3. Selected Bond Lengths (Å) and Bond Angles (deg) for [{(HN*t*Bu)(N*t*Bu)Zr(η^3-L)}$^-${K(η^6-C$_7$H$_8$)}$^+$] (3)

Bond Lengths			
Zr(1)−N(2)	2.207(11)	Zr(1)−N(3)	2.202(11)
Zr(1)−N(4)	2.088(10)	Zr(1)−N(5)	1.893(9)
Zr(1)−N(6)	2.607(8)	P(1)−N(1)	1.767(11)
P(1)−N(2)	1.698(11)	P(1)−N(6)	1.765(11)
P(1)−P(2)	2.654(4)	K(1)−N(1)	2.910(9)
K(1)−N(2)	3.012(13)	K(1)−N(5)	3.069(11)
K(1)−C(71)	3.357(15)	K(1)−C(72)	3.351(16)
K(1)−C(73)	3.334(15)	K(1)−C(74)	3.383(16)
K(1)−C(75)	3.379(17)	K(1)−C(76)	3.389(14)
K(1)−C(14)	3.74	K(1)−C(32)	3.42
K(1)−C(53)	3.23		
Bond Angles			
N(6)−P(1)−N(1))	83.3(5)	N(6)−P(2)−N(1)	82.7(5)
P(1)−N(1)−P(2)	96.3(4)	P(2)−N(6)−P(1)	97.6(4)
C(21)−N(2)−P(1)	118.1(9)	C(21)−N(2)−Zr(1)	132.9(8)
P(1)−N(2)−Zr(1)	105.7(5)	C(31)−N(3)−P(2)	120.7(9)
C(31)−N(3)−Zr(1)	131.6(9)	P(2)−N(3)−Zr(1)	107.5(5)
C(51)−N(5)−Zr(1)	172.4(9)		

indicative of the delocalization of electrons in the N(5)−P(3)−N(6) unit, in agreement with the trigonal planar coordination geometry at N(5) and N(6) (the sum of the angles at N(5) and N(6) are 360.0° and 359.9°), respectively. The bond distances of Zr(1)−N(5) (2.289(2) Å) and Zr(1)−N(6) (2.270(2) Å) are comparable with those of the Zr−N bonds to the PhC(NSiMe$_3$)$_2$ groups (2.284(9) and 2.385(9) Å) found in [{PhC(NSiMe$_3$)$_2$}Zr(η^2-PhCN-SiMe$_3$)(μ-NSiMe$_3$)]$_2$.[13] The chlorine atom may exist in two or more positions; the longest distance of the two possible positions of the chlorine atom is 0.974 Å. The mean Zr(1)−Cl(1) bond length (2.468 Å) is comparable to those found in Cp$_2$ZrCl$_2$ (2.441 Å)[14] and in Cp$_2$ZrCl(η^2-NHNCHSiMe$_3$)·C$_7$H$_8$ (2.5299(9) Å).[15]

The X-ray diffraction analysis of **3** reveals that the five coordination sites at zirconium are occupied by three η^3-L nitrogen atoms, one imido moiety, and one amido ligand, respectively. The bond distances Zr(1)−N(2) (2.207(11) Å), Zr(1)−N(3) (2.202(11) Å), and Zr(1)−N(6) (2.607(8) Å) are slightly longer than those found in **2** (2.089(4), 2.099(3), and 2.568(4) Å) and in [(η^3-L)Zr(μ-NH)]$_2$ (2.116(7), 2.129(7), and 2.399(7) Å), which suggests a single bond property of Zr(1)−N(2) and Zr(1)−N(3). A planar four-membered P(1)N(1)P(2)N(6) ring (the sum of the angles within the ring is 359.9°) is found in **3**. The bond lengths P(1)−N(2) (1.698(11) Å), P(1)−N(1) (1.767(11) Å), and P(1)−N(6) (1.765(11) Å) are comparable with those found in the η^3-L ligand of compound **2** and [(η^3-L)Zr(μ-NH)]$_2$, respectively. The approximately trigonal planar coordination geometry (the sum of the angles at N(2) and N(3) are 356.7° and 359.3°) indicates that the N(2) and N(3) atoms are nearly sp^2 hybridized. The Zr(1)−N(4) (amido) bond distance (2.088(10) Å) is similar with those found in Cp*Zr=NAr(NHAr)·(C$_5$H$_5$N) (2.01 Å) and in Cp*Zr(NH*t*Bu)$_3$ (2.106(5) Å).[6] Due to the formation of the N(5)→K(1) bond, the Zr(1)=N(5) (imido) bond length (1.893(9) Å) is slightly longer than those found in [P$_2$N$_2$]Zr=N*t*Bu ([P$_2$N$_2$] = PhP(CH$_2$SiMe$_2$NSiMe$_2$CH$_2$)$_2$PPh, 1.8413(15) Å),[16] (TTP)Zr=NAr (TTP = *meso*-tetra-*p*-tolylporphyrinato dianion, Ar = 2,6-diisopropylphenyl, 1.863(2) Å),[17] and Cp*Zr=NAr(NHAr)·(C$_5$H$_5$N) (1.876(4) Å).[6]

The K(1)−N(1) (2.910(9) Å), K(1)−N(2) (3.012(13) Å), and K(1)−N(5) (3.069(11) Å) bond lengths are longer than those of K−N bonds found in [KN(SiMe$_3$)$_2$]$_2$ (2.770(3) and 2.803(3) Å),[18] in agreement with the amidoimido zirconium ionic structure in **3**. The distances of K(1) to the carbon atoms on the toluene ring (3.334(15)−3.389(14) Å, av 3.366 Å) are similar to those found in the K(η^6-benzene) complex [(η^6-C$_6$H$_6$)KOSiMe$_2$Ph]$_4$ (3.233(14)−3.308(6) Å, av 3.275 Å).[19] The distance from K(1) to the center of the toluene ring (3.07 Å) is comparable to that found in the K(η^6-toluene) complex [K{Sn[CH$_2$*t*Bu)$_3$}(η^6-C$_7$H$_8$)$_3$] (3.13−3.41 Å, av 3.30 Å).[20] Kebarle and coworkers[21] have calculated the bond energy of benzene to K$^+$ of about 80 kJ mol^{-1}. Interestingly, an additional weak bonding relationship between potassium and three methyl groups (K(1)−C(14) 3.74 Å, K(1)−C(32) 3.42 Å, and K(1)−C(53) 3.23 Å; the distances of K(1) with three protons of these methyl groups are 3.0 Å, respectively) is observed in the structure of **3**. The interactions between K(1) and η^6-C$_7$H$_8$ as well as with three methyl groups are important to stabilize the potassium ion in addition to the K−N contacts.

The X-ray structural investigation of **3** shows that in the anion the zirconium is coordinated to four nitrogen atoms having different Zr−N bond lengths of single and double bond character. The anion is well separated from the K(η^6-C$_7$H$_8$) cation in **3**. Therefore we assume that the negative charge is preferentially delocalized over the whole anion ({(HN*t*Bu)(N*t*Bu)Zr(η^3-L)}$^-$). The resonances of the methyl protons of the *tert*-butyl groups of the η^3-L ligand (δ 1.47−0.98 ppm) in the ^{1}H NMR spectrum of **3** appear at relatively high field compared

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with those found in compound **2** (δ 1.70−1.39 ppm) and [(η^3-L)Zr(μ-NH)]$_2$ (δ 1.58−1.23 ppm), and the methyl protons of the *tert*-butyl group of the imido ligand give rise to two resonances at relatively high field (δ 1.65 and 1.64 ppm) compared with that found in [P$_2$N$_2$]Zr═N*t*Bu (δ 1.75 ppm).[16] The upfield shift of the resonances is caused by the negatively charged anion.

Conclusion

We have shown that the reaction of η^3-bis(*tert*-butylamido)cyclodiphosph(III)azane zirconium chloride with lithiated bis(*tert*-butylamido)cyclodiphosph(III)-azane leads to the cleavage of the two P−N bonds of the L^{2-} group and the formation of (η^3-L)[η^2-(N*t*Bu)$_2$P]-ZrCl (**2**). Further treatment of compound **2** with K/Na alloy in toluene leads to the cleavage of the P−N bonds under simultaneous formation of an amidoimido zirconium anion, [(HN*t*Bu)(N*t*Bu)Zr(η^3-L)]$^-$. Moreover, the reactions yielding **2** and **3** have in common that the P−N bonds are cleaved by either compound **1** or potassium/sodium alloy. The bulky η^3-L, imido, and amido ligands on zirconium are important for forming and stabilizing the amidoimido zirconium monomer **3**, while the interactions between K and amido moieties, the η^6-C_7H_8 ligand, and the three methyl groups are important to stabilize the potassium ion in **3**. Furthermore, compound **3** should be a good precursor for the synthesis of homo- and heterometallic complexes.

Experimental Section

General Data. All experimental manipulations were carried out under an atmosphere of purified nitrogen using standard Schlenk techniques. Samples prepared for spectral measurements as well as for reactions were manipulated in a glovebox. Solvents were dried using conventional procedures, distilled under nitrogen, and degassed prior to use. Deuterated NMR solvents were treated with K/Na alloy, distilled, and stored under nitrogen.

The NMR spectra were recorded on Bruker AM 250 or MSL 500 NMR spectrometers with SiMe$_4$ as external standard. Mass spectra were recorded on a Finnigan MAT 8230 or Varian MAT CH 5 mass spectrometer using the EI-MS method. The most intensive peak of an isotopic distribution is tabulated. IR spectra are recorded on a Bio-Rad FTS-7 spectrometer as Nujol mulls between KBr plates. Elemental analyses were performed at the Analytical Laboratory of the Institute of Inorganic Chemistry, University of Göttingen.

Synthesis of (η^3-L)[η^2-(N*t*Bu)$_2$P]ZrCl (2). A solution of **1** (5.09 g, 10.0 mmol) and L(Li·THF)$_2$ (2.52 g, 5.0 mmol) in toluene (120 mL) was stirred for 48 h at 80 °C. After filtration and concentration in vacuo to 40 mL the resulting yellow solution was stored at 0 °C for one week. Yellow crystals of **2** (3.08 g) were obtained. The concentration of the filtrate to 10 mL and storage at −20 °C for 3 days gave an additional crop of **2** (0.68 g). Total yield: 3.76 g (58%). Mp: 267 °C. IR (Nujol): $\tilde{\nu}$ 2277, 2158, 1959, 1631, 1385, 1219, 1189, 1081, 1037, 983, 881, 844, 819, 777, 721, 587 cm^{-1}. ^{1}H NMR (500 MHz, C_6D_6): δ 1.70, 1.69 (s, 9 H, *tBu*), 1.59 (s, 9 H, *tBu*), 1.49 (s, 18 H, *tBu*), 1.47 (s, 9 H, *tBu*), 1.40,1.39 (s, 9 H, *tBu*). EI-MS: *m/e* (%) 644 (18) (M$^+$), 471 (100) (M$^+$ − (N*t*Bu)$_2$P). Anal. Calcd for $C_{24}H_{54}ClN_6P_3Zr$ (646.33): C, 44.6; H, 8.4; N, 13.0. Found: C, 44.1; H, 8.3; N, 12.5.

Synthesis of [{(HN*t*Bu)(N*t*Bu)Zr(η^3-L)}$^-${K(η^6-C_7H_8)}$^+$] (3). The suspension of **2** (1.94 g, 3.0 mmol) and K/Na alloy (K 0.16 g, 4.1 mmol; Na 0.05 g, 2.2 mmol) in toluene (80 mL) was stirred for 24 h at room temperature and then refluxed for 48 h with stirring. After filtration and concentration in vacuo to 10 mL the resulting brown solution was kept at −20 °C for one week. Yellow crystals of **3** were obtained in 24% yield (0.52 g). Dec pt: 290 °C. IR (Nujol): $\tilde{\nu}$ 3373, 2264, 2193, 1938, 1600, 1382, 1195, 1101, 1032, 1018, 1001, 940, 833, 796, 756, 584 cm^{-1}. ^{1}H NMR (500 MHz, C_6D_6): δ 7.13−6.98 (m, C_6*H_4*), 4.58 (br, N*H*), 2.10 (s, Ph*Me*), 1.65, 1.64 (s, Zr═N*tBu*), 1.47, 1.45, 1.44, 1.43 (s, *tBu*), 1.39 (s, *tBu*), 1.38 (s, *tBu*), 1.31 (s, *tBu*), 1.23 (s, *tBu*), 0.98 (s, *tBu*). EI-MS: *m/e* (%) 618 (3) (M$^+$ − C_7H_8), 39 (100) (K$^+$). Anal. Calcd for $C_{31}H_{63}KN_6P_2Zr$ (712.16): C, 52.2; H, 8.9; N, 11.8. Found: C, 51.6; H, 8.7; N, 11.5.

X-ray Analysis of 2 and 3. Single crystals of **2** and **3** suitable for X-ray structural analysis were obtained from toluene by keeping the reaction mixture at 0 °C and −20 °C for one week, respectively. Data for the structures of **2** and **3** were collected on a Stoe-AED 2 diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). Intensity measurements were performed at 133(2) and 200(2) K on cooled crystals in an oil drop,[22] respectively. The structures were solved by direct methods (SHELXS-97)[23] and refined with all data by full-matrix least-squares on F^2.[24] The hydrogen atoms of the C−H bonds and that of the N−H bond were added in idealized positions. Other details of the data collection, structure solution, and refinement are listed in Table 1.

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Supporting Information Available: Tables of crystal data, fractional coordinates, bond lengths and angles, anisotropic displacement parameters, and hydrogen atom coordinates of **2** and **3** are available free of charge via the Internet at http://pubs.acs.org.

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