The formation of an imidozirconium compound by migration of the imido group from phosphorus to zirconium †

Guangcai Bai, Herbert W. Roesky,* Mathias Noltemeyer and Hans-Georg Schmidt

Institut für Anorganische Chemie der Universität Göttingen, Tammannstrasse 4, D-37077 Göttingen, Germany. E-mail: hroesky@gwdg.de.

The η^3/η^1-bis(*tert*-butylamido)cyclodiphosph(III)azane zirconium chloride $(\eta^3$-L)$(\eta^1$-LH)ZrCl [**1**; L = (PN*t*Bu)$_2$-(N*t*Bu)$_2$] has been synthesized from the reaction of ZrCl$_4$ with LH$_2$ and *n*BuLi in toluene. Further reaction of **1** with K–Na alloy in toluene leads to the cleavage of two P–N bonds of the η^3-L ligand and the migration of the N*t*Bu group from P to Zr, with the formation of the amidoimidozirconium potassium complex [$(\eta^1$-LH)Zr=N*t*Bu-{(N*t*Bu)$_2$PPN*t*Bu}{K·$(\eta^6$-C$_7$H$_8$)}]·0.5C$_7$H$_8$] (**2**). The molecular structures of **1** and **2** have been determined by X-ray diffraction. In the crystalline state of **2** an η^1-L ligand, an imido moiety (N*t*Bu) and two amido nitrogen atoms [η^2-(N*t*Bu)$_2$PPN*t*Bu] bind to the zirconium center, and the coordination sphere of K is occupied by three amido nitrogen atoms [η^3-(N*t*Bu)$_2$PPN*t*Bu], an η^6-C$_7$H$_8$ molecule and two Me groups.

Introduction

The chemistry of group 4 imido complexes continues to attract considerable interest due to their high activities in catalytic processes and stoichiometric reactions, such as C–H bond activation,[1] hydroamination of alkynes and allenes,[2] [2 + 2] cycloaddition,[3] synthesis of heterometallic complexes,[4] and imido group transfer reactions in catalytic processes.[5] A number of ligand systems involving nitrogen-based donors have been explored for such compounds due to their easy preparation, good solubility and steric bulk.[6]

We have been interested for some time in developing group 4 imido chemistry. The first terminal titanium imido complex Ph$_2$P(S)N=TiCl$_2$·3C$_5$H$_5$N was structurally characterized by us in 1990.[7] Moreover, we have already reported the preparation of a series of group 4 metal imido-bridged dinuclear complexes[8] and the monomers with terminal imido ligands.[9] Recently, we were attracted to the bis(*tert*-butylamido)cyclodiphosph(III)azane ligand reported by Stahl *et al.* in 1998.[10] In a recent publication we introduced the synthesis of the first unsubstituted imido (NH) bridged dinuclear zirconium compound [$(\eta^3$-L)Zr(μ-NH)]$_2$ [L = (PN*t*Bu)$_2$(N*t*Bu)$_2$].[11] Furthermore, the amidoimidozirconium potassium ionic complex [{$(\eta^3$-L)Zr=N*t*Bu(HN*t*Bu)}$^-${K·$(\eta^6$-C$_7$H$_8$)}$^+$] was successfully prepared by treatment of $(\eta^3$-L){η^2-(N*t*Bu)$_2$P}ZrCl with Na–K alloy in toluene.[12] In this paper, we describe the synthesis of an η^3/η^1-bis(*tert*-butylamido)cyclodiphosph(III)azane zirconium chloride and an amidoimidozirconium potassium complex.

Results and discussion

Synthesis and characterisation

Treatment of ZrCl$_4$ with 2 equiv. of LH$_2$ and 3 equiv. of *n*BuLi in toluene leads to the formation of the η^3/η^1-bis(*tert*-butyl-amido)cyclodiphosph(III)azane zirconium chloride $(\eta^3$-L)$(\eta^1$-LH)ZrCl (**1**; Scheme 1). Further reaction of **1** with K–Na alloy in toluene yields the amidoimidozirconium potassium complex [$(\eta^1$-LH)Zr=N*t*Bu{(N*t*Bu)$_2$PPN*t*Bu}{K·$(\eta^6$-C$_7$H$_8$)}]·0.5C$_7$H$_8$] (**2**; Scheme 2). In this reaction, cleavage of two P–N bonds of
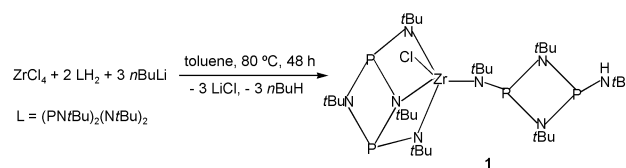
Scheme 1
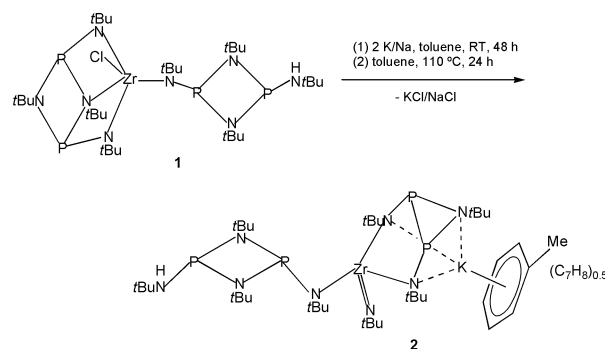
Scheme 2

the η^3-L ligand in **1** by alkali metals results in the formation of a Zr=N double bond, a P–P single bond and K–N bonds. The mechanism is not clear, the zirconium compound **1** seems crucial for the reductive elimination of the *t*BuN group from P. Obviously, the bulky ligands on zirconium are essential for stabilizing the imidozirconium monomer **2**.

Compounds **1** (pale yellow) and **2** (colourless) are crystalline solids. **1** starts to decompose at 255 °C (mp: 288 °C), while **2** is stable above the melting point (273 °C). The IR spectra show a broad absorption (3378 cm^{-1}) and two absorptions (3377 and 3334 cm^{-1}) for **1** and **2**, respectively, assignable to the N–H stretching frequencies. The most intense peak in the EI mass spectrum of **1** appears at *m/z* 471 (M$^+$ − LH), and the signal at 818 (8%) is assigned to the molecular ion. Compound **2** exhibits the fragments (M$^+$ − K − 1.5 C$_7$H$_8$ + H), (M$^+$ − K − 1.5 C$_7$H$_8$ − *t*Bu + H) and (L$^+$ − *t*Bu) at *m/z* 784 (9), 727 (11) and 276 (100%). While the signal at *m/z* 915 (M$^+$ − 0.5 C$_7$H$_8$) was observed with very low intensity due to the easy loss of the C$_7$H$_8$ molecule (no bonding relationship with K) under EI-MS

conditions in the spectrum of compound **2**. The ^{1}H NMR spectral data of **1** and **2** are consistent with their structures. The methyl protons of the *tert*-butyl groups give rise to seven resonances for **1** (δ 1.94 to 1.19 ppm) and **2** (δ 1.94 to 1.11 ppm). The resonances of the NH proton appear as two singlets for **1** (δ 3.30 and 3.28 ppm) and **2** (δ 3.38 and 3.34 ppm). The elemental analysis of **2** shows that the C and H contents are slightly lower than the calculated values due to its sensitivity to moisture and the partial removal of the toluene molecule from the crystalline solid *in vacuo*.

X-Ray crystallographic studies of 1 and 2

The molecular structures of **1** and **2** are shown in Fig. 1 and 2,
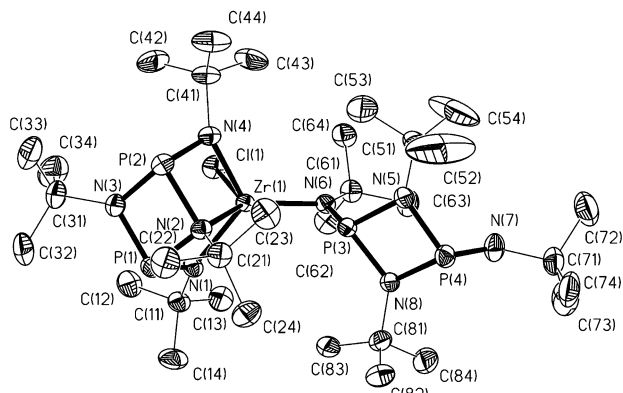

Fig. 1 Molecular structure of $(\eta^3\text{-L})(\eta^1\text{-LH})\text{ZrCl}$ (**1**) (50% probability ellipsoids. H atoms bonded to C and N are omitted for clarity).
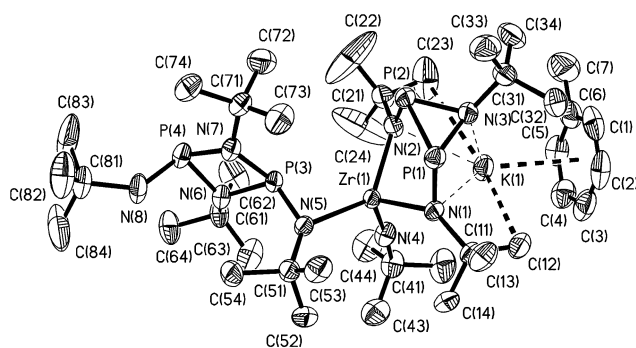

Fig. 2 Molecular structure of $[(\eta^1\text{-LH})\text{Zr}=\text{N}t\text{Bu}\{(\text{N}t\text{Bu})_2\text{PPN}t\text{Bu}\}$-$\{\text{K}\cdot(\eta^6\text{-C}_7\text{H}_8)\}]\cdot0.5\text{C}_7\text{H}_8$ (**2**) (50% probability ellipsoids. The half molecule of toluene and H atoms bonded to C and N are omitted for clarity).

with selected bond lengths and angles in Tables 1 and 2. Details of the data collection, structure solution and refinement are given in Table 3.

Compounds **1** and **2** crystallize in the monoclinic and triclinic space groups $P2_1/n$ and $P\bar{1}$, respectively. The molecular structure of crystalline **1** shows that one η^3-L ligand, one η^1-LH group and one chlorine atom complete the coordination sphere of Zr. The chlorine atom is tilted away from the N(2)*t*Bu moiety and the η^1-LH ligand, which minimizes the steric repulsion between the Cl atom and the N(2)*t*Bu group as well as the η^1-LH ligand. The bond lengths Zr(1)–N(1) [2.104(2)], Zr(1)–N(4) [2.103(7)] and Zr(1)–N(2) [2.376(2) Å] are comparable with those found in $[(\eta^3\text{-L})\text{Zr}(\mu\text{-NH})]_2$ [2.116(7), 2.129(7) and 2.377(7) Å, respectively][11] and $(\eta^3\text{-L})\{\eta^2\text{-(N}t\text{Bu})_2\text{P}\}\text{ZrCl}$ [2.091(2), 2.099(2) and 2.568(2) Å, respectively][12] The approximately trigonal planar coordination at N(1) and N(4) [the sum of the angles at N(1) and at N(4) is 359.2°] indicates that these atoms are nearly sp² hybridized and donate their lone pairs of electrons into the empty d-orbitals of zirconium as 3-electron donors, in analogy to the bonding situation in $[(\eta^3\text{-L})\text{Zr}(\mu\text{-NH})]_2$ and $(\eta^3\text{-L})\{\eta^2\text{-(N}t\text{Bu})_2\text{P}\}\text{ZrCl}$. The bond lengths

Table 1 Selected bond lengths (Å) and angles (°) for $(\eta^3\text{-L})(\eta^1\text{-LH})\text{ZrCl}$ (**1**)

Zr(1)–N(1)	2.104(2)	Zr(1)–N(2)	2.376(2)
Zr(1)–N(4)	2.103(2)	Zr(1)–N(6)	2.210(2)
Zr(1)–Cl(1)	2.4723(8)	P(1)–N(1)	1.698(2)
P(1)–N(3)	1.730(2)	P(1)–N(2)	1.785(2)
P(1)–P(2)	2.6594(11)	P(3)–P(4)	2.6181(10)
P(3)–N(5)	1.716(2)	P(3)–N(6)	1.629(2)
P(3)–N(8)	1.719(2)	P(4)–N(7)	1.668(2)
N(1)–Zr(1)–N(6)	122.48(8)	N(1)–Zr(1)–N(2)	67.37(8)
N(4)–Zr(1)–N(6)	124.46(8)	N(4)–Zr(1)–Cl(1)	88.66(7)
N(1)–Zr(1)–Cl(1)	89.62(7)	N(6)–Zr(1)–Cl(1)	90.63(6)
N(2)–P(2)–N(3)	81.64(11)	N(2)–P(1)–N(3)	81.76(11)
P(2)–N(2)–P(1)	96.31(11)	P(1)–N(3)–P(2)	100.28(12)
N(5)–P(3)–N(8)	81.17(11)	N(5)–P(4)–N(8)	80.32(11)
P(3)–N(5)–P(4)	98.92(12)	P(3)–N(8)–P(4)	98.53(11)
N(7)–P(4)–N(5)	105.98(12)	N(7)–P(4)–N(8)	106.40(12)
P(1)–N(1)–Zr(1)	103.81(11)	C(11)–N(1)–P(1)	117.99(18)
C(11)–N(1)–Zr(1)	137.17(18)	P(3)–N(6)–Zr(1)	87.02(10)
C(61)–N(6)–P(3)	133.78(19)	C(61)–N(6)–Zr(1)	139.20(17)

Table 2 Selected bond lengths (Å) and angles (°) for $[(\eta^1\text{-LH})\text{Zr}=\text{N}t\text{Bu}\{(\text{N}t\text{Bu})_2\text{PPN}t\text{Bu}\}\{\text{K}\cdot(\eta^6\text{-C}_7\text{H}_8)\}]\cdot0.5\text{C}_7\text{H}_8$ (**2**)

Zr(1)–N(1)	2.167(3)	Zr(1)–N(2)	2.194(3)
Zr(1)–N(4)	1.864(3)	Zr(1)–N(5)	2.263(3)
P(1)–N(1)	1.689(3)	P(1)–N(3)	1.774(3)
P(1)–P(2)	2.236(2)	P(3)–P(4)	2.626(2)
N(1)–K(1)	3.086(3)	N(2)–K(1)	2.859(3)
N(3)–K(1)	2.892(4)	C(1)–K(1)	3.406(5)
C(2)–K(1)	3.302(5)	C(3)–K(1)	3.260(5)
C(4)–K(1)	3.311(5)	C(5)–K(1)	3.417(5)
K(1)–C(6)	3.466(5)	K(1)–C(c)[a]	3.07
K(1)–C(12)	3.14	K(1)–C(23)	3.30
P(3)–N(5)	1.618(3)	P(3)–N(6)	1.734(3)
P(3)–N(7)	1.745(3)	P(4)–N(8)	1.671(3)
N(1)–Zr(1)–N(4)	105.06(13)	N(1)–Zr(1)–N(2)	94.33(12)
N(4)–Zr(1)–N(5)	112.54(13)	N(2)–Zr(1)–N(5)	130.17(11)
P(1)–N(1)–Zr(1)	102.48(13)	Zr(1)–N(1)–C(11)	139.1(2)
P(1)–N(1)–C(11)	117.2(2)	P(2)–N(2)–Zr(1)	102.10(14)
Zr(1)–N(2)–C(21)	134.3(2)	P(2)–N(2)–C(21)	118.4(2)
N(6)–P(4)–N(7)	80.58(14)	N(6)–P(3)–N(7)	80.30(14)
P(4)–N(7)–P(3)	97.95(15)	P(4)–N(6)–P(3)	98.41(15)
N(7)–P(4)–P(3)	41.16(10)	P(3)–N(5)–Zr(1)	89.47(12)
C(51)–N(5)–P(3)	133.9(2)	C(51)–N(5)–Zr(1)	136.39(19)

[a] C(c) represents the center of the C_7H_8 ring.

P(1)–N(1) [1.698(2)], P(1)–N(3) [1.730(2)] and P(1)–N(2) [1.785(2) Å] are similar to those found in $[(\eta^3\text{-L})\text{Zr}(\mu\text{-NH})]_2$ [1.686(8), 1.733(8) and 1.789(8) Å, respectively], $(\eta^3\text{-L})\{\eta^2\text{-(N}t\text{Bu})_2\text{P}\}\text{ZrCl}$ [1.698(2), 1.744(2) and 1.777(2) Å, respectively], and in $[(\eta^3\text{-L})\text{In}]_2$ [1.670(3), 1.723(3) and 1.801(3) Å, respectively].[13] The sp² hybridized N(6) atom [the sum of the angles at N(6) is 360.0°] results in a Zr(1)–N(6) bond length [2.210(2) Å] similar to those of Zr(1)–N(1) and Zr(1)–N(4), and of the Zr–N bonds to the (N*t*Bu)_2P group in $(\eta^3\text{-L})\{\eta^2\text{-(N}t\text{Bu})_2\text{P}\}\text{ZrCl}$ [2.289(2) and 2.270(2) Å]. The Zr(1)–N(6) bond distance is also comparable with those found in Cp*ZrMe_2{(2,6-*i*Pr_2C_6H_3)-N(SiMe_3)} [2.104(2) Å][14] and Cp*_2Zr(NHPh)_2 [2.117(3) and 2.124(3) Å].[15] Almost identical P(3)–N(5) [1.716(2)] and P(3)–N(8) [1.719(2) Å] bond lengths were found in the η^1-L ligand in **1**, and they are within the range of those found in aminophosphines R_2N–PR_2 (1.60 to 1.78 Å).[16] The formation of the N(2) → Zr(1) donor bond results in the distortion of the P(1)N(2)P(2)N(3) four-membered ring of the η^3-L ligand (the sum of the angles within the ring is 348.99°), while the η^1-L ligand contains a nearly planar P(3)N(5)P(4)N(8) four-membered ring (the sum of the angles within the ring is 358.94°).

The X-ray diffraction analysis of **2** reveals that the four coordination sites at zirconium are occupied by an η^1-L ligand, an imido moiety and two amido nitrogen atoms. The bond

Table 3 Crystallographic data for **1** and **2**

Complex	**1**	**2**
Empirical formula	$C_{32}H_{73}ClN_8P_4Zr$	$C_{32}H_{73}KN_8P_4Zr \cdot 1.5C_7H_8$
Fw	820.53	824.21 + (1.5 × 92.14)
Crystal size/mm	0.4 × 0.4 × 0.4	1.2 × 0.3 × 0.2[d]
Crystal system	Monoclinic	Triclinic
Space group	$P2_1/n$	$P\bar{1}$
a/Å	14.7679(16)	11.070(6)
b/Å	19.227(3)	13.937(12)
c/Å	15.448(2)	18.628(15)
α/°	90	72.35(6)
β/°	91.732(12)	85.56(5)
γ/°	90	82.79(6)
Cell volume V/Å^3	4384.4(10)	2715(3)
Z	4	2
ρ_c/g mm^{-3}	1.243	1.177
μ/mm^{-1}	0.489	0.432
$F(000)$	1752	1030
2θ range/°	7.26–50.04	7.06–50.00
Data measured, unique (R_{int})	7716, 7716 (0.0)	16403, 9538 (0.0511)
R,[a] $wR2$[b] [$I > 2\sigma(I)$]	0.0372, 0.0792	0.0453, 0.1018
R, $wR2$ (all data)	0.0495, 0.873	0.0647, 0.1135
Goodness of fit, S[c]	1.076	1.061
Refined parameters	439	546
Restraints	0	624[e]
Largest diff. peak, hole/e Å^{-3}	+0.054, −0.424	+0.661, −0.568

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)]^{1/2}$. [c] $S = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma(n - p)]^{1/2}$. [d] Could not be cut. [e] Restraints have been used to obtain more equations.

lengths Zr(1)–N(5) [2.263(3)], P(3)–N(5) [1.618(3)], P(3)–N(6) [1.734(3)] and P(3)–N(7) [1.745(3) Å], as well as the P(3)–P(4) distance [2.626(2) Å] in the η^1-LH ligand are comparable with those found in the η^1-LH ligand of compound **1** [2.210(2), 1.629(2), 1.716(2), 1.719(2) and 2.618(10) Å, respectively]. A slightly distorted P(3)N(6)P(4)N(7) four-membered ring (the sum of the angles in the ring is 357.24°) was found in **2**.

The Zr(1)–N(4) (imido) bond length [1.864(3) Å] is comparable with those found in [{(η^3-L)Zr=NtBu(HNtBu)}$^-${K·(η^6-C_7H_8)}$^+$] [1.893(9)][12] and Cp*CpZr=NtBu·THF [1.846(2) Å].[17] The P(1)–P(2) bond length [2.236(2) Å] is comparable with the P–P distance (2.234 Å) in black phosphorus[18] and those found in polyphosphides (2.215 to 2.230 Å).[19] The K(1)–N(2) [2.859(3)] and K(1)–N(3) [2.892(4) Å] bond lengths are comparable with those in [KN(SiMe$_3$)$_2$]$_2$ [2.770(3) and 2.803(3) Å, respectively][20] and [K(NPPh$_3$)]$_6$·4C$_7$H$_8$ [2.691(5) to 2.975(5) Å, respectively; avg. 2.805 Å],[21] and are shorter than those in the ionic complex [{(η^3-L)Zr=NtBu(HNtBu)}$^-${K·(η^6-C$_7$H$_8$)}$^+$] [2.910(9), 3.012(13) and 3.069(11) Å].[12] The relatively long K(1)–N(1) [3.086(3) Å] bond length indicates only a weak interaction between N(1) and K(1). Furthermore, the approximately trigonal planar coordination geometry [the sums of the angles at N(1) and N(2) are 359.3 and 354.8°, respectively] shows that the N(1) and N(2) atoms are nearly sp^2 hybridized; N(1) and N(2) donate their lone-pair electrons into the empty d-orbitals of zirconium and the s-orbital of potassium as 3-electron donors. Due to the formation of N–K bonds, the Zr(1)–N(1) [2.167(3)] and Zr(1)–N(2) [2.194(3) Å] bond lengths are longer than those found in [(η^3-L)Zr(μ-NH)]$_2$ [2.116(7)] and (η^3-L)(η^1-LH)ZrCl [2.104(2) Å].

The distances from K(1) to the carbon atoms of the toluene ring [3.260(5) to 3.466(5) Å, avg. 3.359 Å] are similar to those in the K·(η^6-benzene) complexes [(η^6-C$_6$H$_6$)·KOSiMe$_2$Ph]$_4$ [3.233(14) to 3.308(6) Å, avg. 3.275 Å][22] and L'K·C$_7$H$_8$ [L' = 18-crown-6, 3.044(5) to 3.311(5) Å].[23] The distance from K(1) to the centroid of the toluene ring (3.07 Å) is comparable to those reported in [K{Sn(CH$_2$tBu)$_3$}·3(η^6-C$_7$H$_8$)] (3.13 to 3.41 Å, avg. 3.30 Å)[24] and Lu{CH(SiMe$_3$)$_2$}$_3$(μ-Cl)K·3(η^6-C$_7$H$_8$) (3.003 and 3.128 Å).[25] Interestingly, an additional weak bonding relationship between potassium and two methyl groups [K(1)–C(12) 3.14, K(1)–C(23) 3.30 Å] is observed in the structure of **2**, in analogy to the K···Me attractions in [iPr$_2$NK·TMEDA]$_2$

(TMEDA = N,N,N',N'-tetramethylethylenediamine; K–C 3.34 to 3.47 Å)[26] and KC(SiMe$_3$)$_2$(SiMe$_2$NMe$_2$) (K–C 3.11 to 3.49 Å).[27] The interactions between K(1) and η^6-C$_7$H$_8$, as well as with the two methyl groups, provide additional stabilization of the potassium ion, additionally to the K–N contacts.

Conclusion

In this study, we have shown that treatment of η^3/η^1-bis(tert-butylamido)cyclodiphosph(III)azane zirconium chloride with K/Na alloy in toluene leads to reductive elimination of a tBuN group with the simultaneous formation of a P–P and a Zr=NtBu bond. It is assumed that the bulky η^1-L, imido and η^2-amido ligands at the zirconium are important for the formation and stabilization of the imido zirconium monomer **2**, while the interaction between K, amido moieties and η^6-C$_7$H$_8$, as well as the agostic interaction with the two methyl groups are important for the stabilization of the potassium ion in **2**. Furthermore, compound **2** should be a good precursor for the synthesis of homo- and heterometallic complexes.

Experimental

General data

All experimental manipulations were carried out under an atmosphere of purified nitrogen using standard Schlenk techniques. Samples prepared for spectral measurements and reactions were manipulated in a glove box. 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 Finnigan MAT 8230 or Varian MAT CH 5 mass spectrometers using the EI-MS method. Only the most intense peak of an isotopic distribution is reported. IR spectra were recorded on a Bio-Rad FTS-7 spectrometer from Nujol mulls between KBr plates. Elemental analyses were performed at the Analytical Laboratory of the Institute of Inorganic Chemistry, University of Göttingen.

Synthesis

(η³-L)(η-LH)ZrCl (1). *n*BuLi (2.5 M in hexane, 14.6 mL, 36.5 mmol) was added to a suspension of ZrCl$_4$ (2.83 g, 12.1 mmol) and LH$_2$ (8.45 g, 24.3 mmol) in toluene (150 mL) at 0 °C. The mixture was warmed to room temperature and then stirred for 48 h at 80 °C. After filtration and concentration *in vacuo* to 40 mL, the resulting yellow solution was stored at −20 °C. Yellow crystals were obtained. Recrystallization of the crystals in toluene afforded pale yellow crystals of **1**. Yield: 48% (3.80 g). Mp: 288 °C (dec.). IR (Nujol, cm^{-1}): $\tilde{\nu}$ = 3378w, 3130w br, 1625m br, 1261m, 1219s, 1192s, 1070s, 1014s, 989m, 928m, 877s, 850m, 819s, 724s, 592m. ^{1}H NMR (500 MHz, C$_6$D$_6$): δ 3.20, 3.28 (br s, 1 H, NH), 1.94 (s, 9 H, *t*Bu), 1.68 (s, 18 H, *t*Bu), 1.54 (s, 9 H, *t*Bu), 1.51 (s, 18 H, *t*Bu), 1.31 (s, 9 H, *t*Bu), 1.19 (ds, 9 H, *t*Bu). EI-MS *m/z* (%): 818 (8) (M$^+$), 471 (100) (M$^+$ − LH). Anal. calcd for C$_{32}$H$_{73}$ClN$_8$P$_4$Zr (820.5): C, 46.8; H, 9.0; N, 13.7; found: C, 46.1; H, 8.8; N, 13.0%.

[(η¹-LH)Zr=N*t*Bu{(N*t*Bu)$_2$PPN*t*Bu}{K·(η⁶-C$_7$H$_8$)}·0.5C$_7$H$_8$] (2). A suspension of **1** (1.64 g, 2.0 mmol) and K–Na alloy (K 0.11 g, 2.8 mmol; Na 0.03 g, 1.3 mmol) in toluene (80 mL) was stirred for 48 h at room temperature and then refluxed for 24 h with stirring. After filtration and concentration *in vacuo* to 10 mL, the resulting brown solution was kept at −20 °C for one week. Colourless crystals of **2** were obtained. Yield: 28% (0.54 g). Mp: 273 °C. IR (Nujol, cm^{-1}): $\tilde{\nu}$ = 3377m, 3334m, 3243w, br, 1605m, 1361s, 1220vs, 1120s, 1087s, 1057s, 1029s, 998s, 920m, 876m, 822m, 804m, 727m, 694m, 661m, 625m. ^{1}H NMR (500 MHz, C$_6$D$_6$): δ 3.38, 3.34 (br s, 1 H, NH), 1.94 (s, 9 H, *t*Bu), 1.69 (s, 18 H, *t*Bu), 1.60 (s, 18 H, *t*Bu), 1.40 (s, 9 H, *t*Bu), 1.28, 1.27 (s, 9 H, *t*Bu), 1.11 (s, 9 H, *t*Bu). EI-MS *m/z* (%): 915 (0.2) (M$^+$ − 0.5 C$_7$H$_8$), 784 (9) (M$^+$ − K − 1.5 C$_7$H$_8$ + H), 727 (11) (M$^+$ − K − 1.5 C$_7$H$_8$ − *t*Bu + H), 276 (100) (L$^+$ − N*t*Bu). Anal. calcd for C$_{42.5}$H$_{85}$KN$_8$P$_4$Zr (962.4): C, 53.0; H, 8.9; N, 11.6; found: C, 51.7; H, 8.7; N, 11.3%.

X-Ray analyses of 1 and 2

Single crystals of **1** and **2** suitable for X-ray structural analysis were obtained from toluene by keeping the reaction mixtures at 0 and −20 °C, respectively, for one week. Data for the structures of **1** and **2** 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, respectively, on cooled crystals in an oil drop.[28] The structures were solved by direct methods (SHELXS-97)[29] and refined with all data by full-matrix least-squares on F^2.[30] The hydrogen atoms of the C–H and N–H bonds were added in idealized positions. Other details of the data collection, structure solution and refinement are listed in Table 3.

CCDC reference numbers 178315 and 178316.

See http://www.rsc.org/suppdata/dt/b2/b200970f/ for crystallographic data in CIF or other electronic format.

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