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Neutral and Anionic Monomeric Zirconium Imides Prepared via Selective C=N Bond Cleavage of a Multidentate and Sterically Demanding β-Diketiminato Ligand

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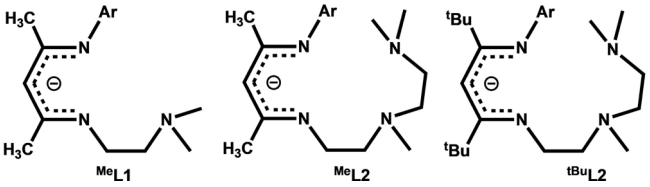
Abstract: A sterically encumbering multidentate β-diketiminato ligand, ^{tBu}L2 (^{tBu}L2=[ArNC(*t*Bu)CHC(*t*Bu)NCH$_2$CH$_2$N(Me)-CH$_2$CH$_2$NMe$_2$]$^-$, Ar = 2,6-*i*Pr$_2$C$_6$H$_3$), is reported in this study along with its coordination chemistry to zirconium(IV). Using the lithio salt of this ligand, Li(^{tBu}L2) (**4**), the zirconium(IV) precursor (^{tBu}L2)ZrCl$_3$ (**6**) could be readily prepared in 85% yield and structurally characterized. Reduction of **6** with 2 equiv of KC$_8$ resulted in formation of the terminal and mononuclear zirconium imide-chloride [C(*t*Bu)CHC(*t*-Bu)NCH$_2$CH$_2$N(Me)CH$_2$CH$_2$NMe$_2$]Zr(=NAr)(Cl) (**7**) as the result of reductive C=N cleavage of the imino fragment in the multidentate ligand ^{tBu}L2 by an elusive Zr^{II} species (^{tBu}L2)ZrCl (**A**). The azabutadienyl ligand in **7** can be further reduced by 2 e$^-$ with KC$_8$ to afford the anionic imide [K(THF)$_2$]{[CH(*t*Bu)CHC(*t*Bu)NCH$_2$CH$_2$N(Me)CH$_2$CH$_2$N(Me)CH$_2$]-Zr=NAr} (**8-2THF**) in 42% isolated yield. Complex **8-2THF** results from the oxidative addition of an amine C–H bond followed by migration to the vinylic group of the formal [C(*t*Bu)CHC(*t*Bu)NCH$_2$CH$_2$N(Me)CH$_2$CH$_2$NMe$_2$]$^-$ ligand in **7**. All halides in **6** can be replaced with azides to afford (^{tBu}L2)Zr(N$_3$)$_3$ (**9**) which was structurally characterized, and reduction with two equiv of KC$_8$ also results in C=N bond cleavage of ^{tBu}L2 to form [C(*t*Bu)CHC(*t*Bu)NCH$_2$CH$_2$N-(Me)CH$_2$CH$_2$NMe$_2$]Zr(=NAr)(N$_3$) (**10**), instead of the expected azide disproportionation to N^{3-} and N$_2$. Solid-state single crystal structural studies confirm the formation of mononuclear and terminal zirconium imido groups in **7**, **8-Et$_2$O**, and **10** with Zr=NAr distances being 1.8776(10), 1.9505(15), and 1.881(3) Å, respectively.

Introduction

Whereas the ubiquitous β-diketiminato ligand has popularized the coordination sphere for early-transition metals,[1] multidentate[2–7] and macrocyclic[8] β-diketiminato scaffolds are now setting the stage as unique ligands that allow for the stabilization of the reactive metal fragments containing metal-ligand multiple bonds. Specifically, this ligand class has been demonstrated to support highly polarized, and terminal imido species[3] with even highly electropositive such as Sc^{3+}; an ion which falls along the demarcation line between transition metal and rare-earth. To this end, the Chen group has reported two multidentate ligands possessing the β-diketiminato scaffold, namely the tridentate ^{Me}L1 (^{Me}L1 = [ArNC(Me)CHC(Me)NCH$_2$CH$_2$N(Me)$_2$]$^-$, Ar = 2,6-*i*Pr$_2$C$_6$H$_3$)[2] and tetradentate ^{Me}L2 (^{Me}L2 = [ArNC(-Me)CHC(Me)NCH$_2$CH$_2$N(Me)CH$_2$CH$_2$NMe$_2$]$^-$, Ar = 2,6-*i*Pr$_2$C$_6$H$_3$)[3,4]



Scheme 1. Multidentate ligands having the β-diketiminato motif, where Ar represents *i*Pr$_2$C$_6$H$_3$.

cartoons depicted in Scheme 1. Part of the reasoning for assembling these ligand scaffolds has been to coordinatively saturate the electropositive metal ion, block aggregation,[9] and prevent ligand disproportionation reactions[10] while maintaining a low-charge to allow for dianionic ligand substitution reactions, namely a highly nucleophilic moiety such as an imide. Only in certain exceptions,[11] there is evidence for irreversible degradation of the β-diketiminato ligand.[12] The use of pendant amino groups on these multidentate ligands stems from the fact that scandium imides[3] can be generated or trapped with donor ligands such as pyridine or pyridine derivatives (e.g. DMAP) as exemplified by the work of Mindiola,[13] Cui,[14] Piers,[15] and more recently, Mountford.[16]

In this study, we wish to report the synthesis of a multidentate variant to the original systems ^{Me}L1 and ^{Me}L2,[2,4] namely a ligand ^{tBu}L2 having *t*Bu groups at the β-carbon positions of the [NCCCN] skeleton in the β-diketiminato framework (Scheme 1). In addition to obtaining and structurally characterizing a non-solvento salt Li(^{tBu}L2), we also showcase how this multidentate

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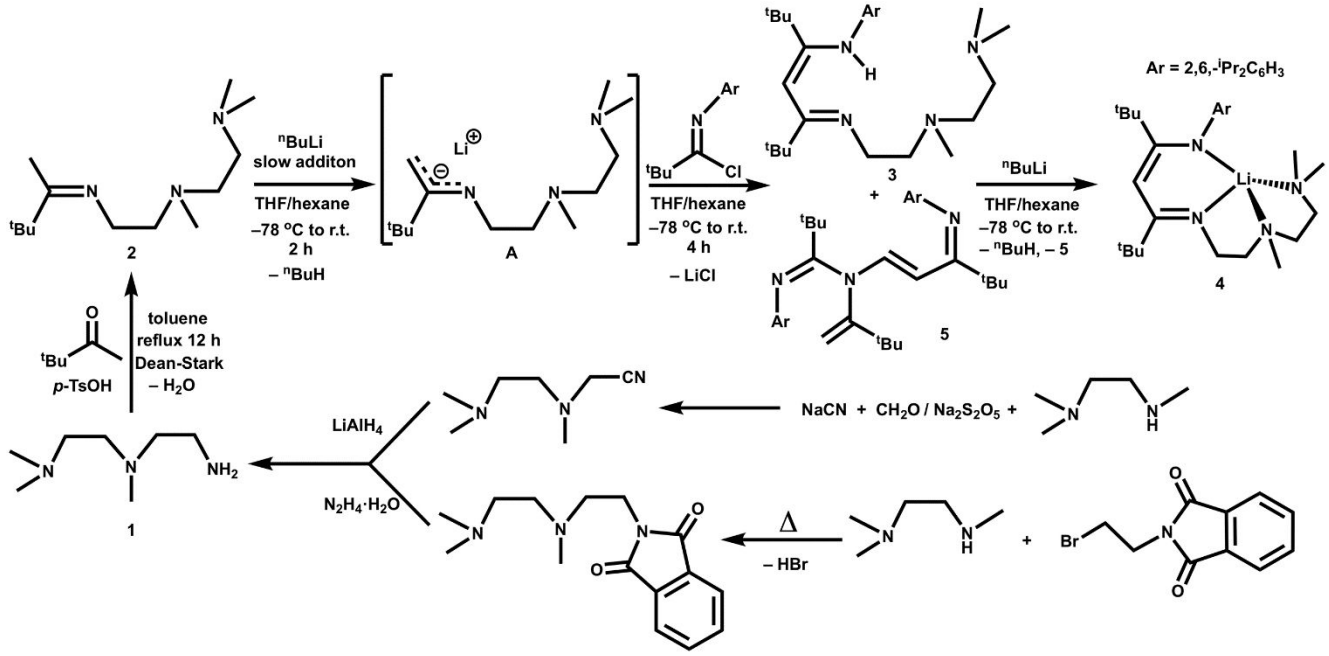
ligand can grip onto Zr^{IV} by making a mononuclear trichlorido precursor, the latter which can be reduced with $2e^-$ or $4e^-$ to make mononuclear Zr imides in neutral or anionic forms. Akin to the chemistry found for the prototypical β-diketiminato ligand,[17] we now report a bulkier ligand ^{tBu}L2 that serves as an intramolecular imide transfer source when reducing Zr^{IV} to Zr^{II}. We demonstrate how this new tetradentate and monoanionic ligand can be transformed to either a multidentate azabutadienyl by $2e^-$ reduction or an unprecedented multidentate trianionic ligands by virtue of $4e^-$ reduction chemistry. Lastly, we show how the replacement of chlorides for azides does not impede the cleavage of the C=N bond when a similar Zr^{IV} precursor is reduced by two electrons.

Results and Discussion

Following the procedure reported in the literature,[18] the *N*′-(2-aminoethyl)-*N*′,*N*,*N*-trimethylethan-1,2-diamine precursor $[Me_2NCH_2CH_2N(Me)CH_2CH_2NH_2]$ (**1**) was prepared accordingly by $LiAlH_4$ reduction of the nitrile precursor $[Me_2NCH_2CH_2N(Me)CH_2CN]$ as documented by Glaser and coworkers (Scheme 2). This procedure results in greater yields of **1** as opposed to an alternative process where the *N*-(2-bromoethyl)phthalimide is treated with *N*,*N*,*N*′-trimethylethylenediamine followed by reduction of the product *N*-(2-bromoethyl)phthalimide with $N_2H_4{\cdot}H_2O$[19] (Scheme 2). Although both protocols to form **1** involve a two-step process stemming from commercially available *N*,*N*,*N*′-trimethylethylenediamine, the reaction between *N*-(2-bromoethyl)phthalimide and *N*,*N*,*N*′-trimethylethylenediamine results in lower yields of phthalimide protected precursor *N*-(2-*N*,*N*,*N*′-trimethylethylenediamine-ethyl)-phthalimide[17] (Scheme 2). Consequently, we prefer the synthesis of the nitrile precursor $[Me_2NCH_2CH_2N(Me)CH_2CN]$ followed by reduction with $LiAlH_4$ to produce **1**.

Using compound **1** as our starting point one can condense it with 3,3-dimethyl-2-butanone $tBuC(O)CH_3$ in the presence of a catalytic amount of *p*-TsOH·H_2O (ca. 0.1 equiv) to afford the imine $[Me_2NCH_2CH_2N(Me)CH_2CH_2N=C(tBu)CH_3]$ (**2**) (Scheme 2). Akin to the protocol used for the preparation of Budzelaar's [ArNHC(*t*Bu)CHC(*t*Bu)NAr] (Ar = 2,6-*i*Pr$_2$C$_6$H$_3$),[20] compound **2** was first deprotonated via slow addition of Li*n*Bu. The reaction most likely traverses through the salt Li$\{Me_2NCH_2CH_2N(CH_3)CH_2CH_2NC(tBu)CH_2\}$ (**A**), which is then quenched with the chloroimine *t*BuC(NAr)Cl[20] (Scheme 2). However, unlike the reported preparation of [ArNHC(*t*Bu)CHC(*t*-Bu)NAr],[20] deprotonation of the imine methyl in **2** does not require the need of TMEDA encapsulated $LiCH_3$ or Li*n*Bu to form a more powerful base. After quenching of **A** with *t*BuC(NAr)Cl, an oily residue and a yellow solid could be separated by work-up of the reaction. The ^{1}H NMR spectrum (Figure S4) of the oil revealed formation of [ArNHC(*t*Bu)CHC(*t*-Bu)$NCH_2CH_2N(Me)CH_2CH_2NMe_2$], defined as H(^{tBu}L2) (**3**), but accompanied with formation of at least two other major side-products which we could not identify (Scheme 2). Attempts to purify **3** from the crude reaction mixture were hampered given the presence of several species in the mixture. Examination of the yellow solid by NMR spectroscopy (vide supra) revealed formation of the lithio salt Li{ArNC(*t*Bu)CHC(*t*-Bu)$NCH_2CH_2N(Me)CH_2CH_2NMe_2$} defined as Li(^{tBu}L2) (**4**), which was formed from the deprotonation of H(^{tBu}L2) (**3**). As a result, we resorted to deprotonating **3** without purification to obtain the precipitate **4**, isolated as a yellow powder in 48% yield in three-steps from **2**. Gratifyingly, deprotonation of the crude **3** still allows isolation of pure **4** thus leaving behind the other neutral side products formed from the reaction of **A** with the



Scheme 2. Synthetic entry to the lithio salt **4** of the β-diketiminato ligand ^{tBu}L2 starting from the trisamino precursor **1**, which can be prepared by two separate reactions stemming from *N*,*N*,*N*′-trimethylethylenediamine.

electrophile *t*BuC(NAr)Cl. After separation and washing of the salt **4**, the pentane filtrate can be concentrated which resulted in the deposit of a small amount of colorless crystals of the triazatetraene [ArNC(*t*Bu)NC(CH_2)C(*t*Bu)CHCHC(*t*Bu)NAr] (**5**). We propose **5** to be a side-product that likely results from the deprotonation and degradation of the ethylene group in **2** as well as the addition of the *t*BuC(NAr)$^+$ carbonium to the nucleophilic nitrogen in a species such as **A** (Scheme 2). Figure 1 (bottom) depicts a solid-state structural diagram of **5**, a species we propose to be one of the side-products of the reaction between **A** and the chloroimine *t*BuC(NAr)Cl. Since compound **5** is formed in a very low yield and is not relevant to our subsequent studies reported herein no further characterization of this side-product nor the other organic material spectroscopically observed in solution was pursued.

The NMR spectra of **4** display asymmetric features for the β-diketiminato scaffold in the ^{tBu}L2 ligand, such as two inequivalent *t*Bu groups at 1.34 and 1.39 ppm in the ^{1}H NMR spectrum. The ^{7}Li NMR spectrum confirmed the presence of Li^+ at 1.73 ppm. In addition to spectroscopic data and to conclusively establish the connectivity of the ligand precursor **4**, an XRD (X-ray diffraction) study on a single crystal grown from pentane at −35 °C was performed. As shown on the top of Figure 1, the solid-state structure of **4** reveals a lithium ion encapsulated by tetradentate ligand. Distortion of the lithium from an idealized tetrahedral geometry to trigonal pyramid is evident given the planarity of N1, N3 and N4 and small deviation of the Li atom from such an imaginary plane (N1-N3-N4), 0.235 Å (τ_4 = 0.65).[21]

Having the lithio salt **4** in hand, we conducted a transmetallation reaction with $ZrCl_4(THF)_2$ in toluene at room temperature. After mixing the two reagents and subsequent work-up of the mixture, the zirconium trichlorido complex (^{tBu}L2)$ZrCl_3$ (**6**) was isolated in 85% yield as a pale yellow solid (Scheme 3).

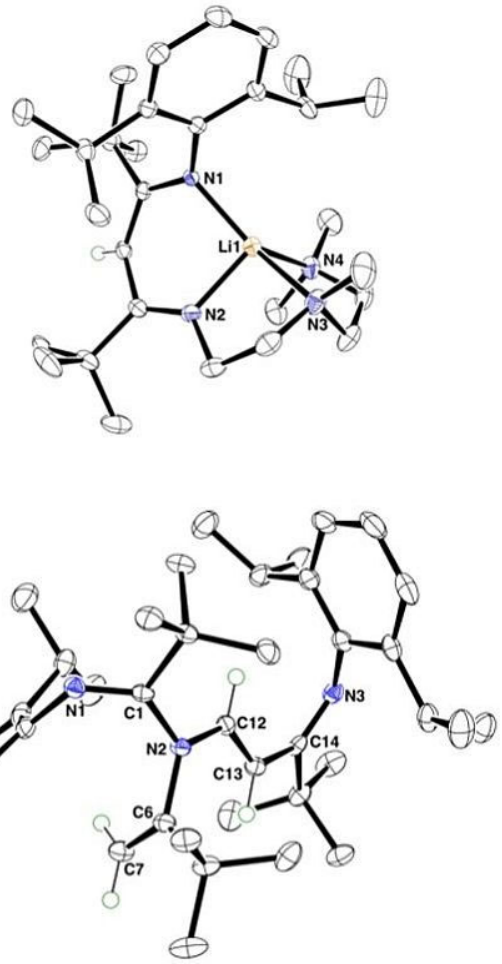
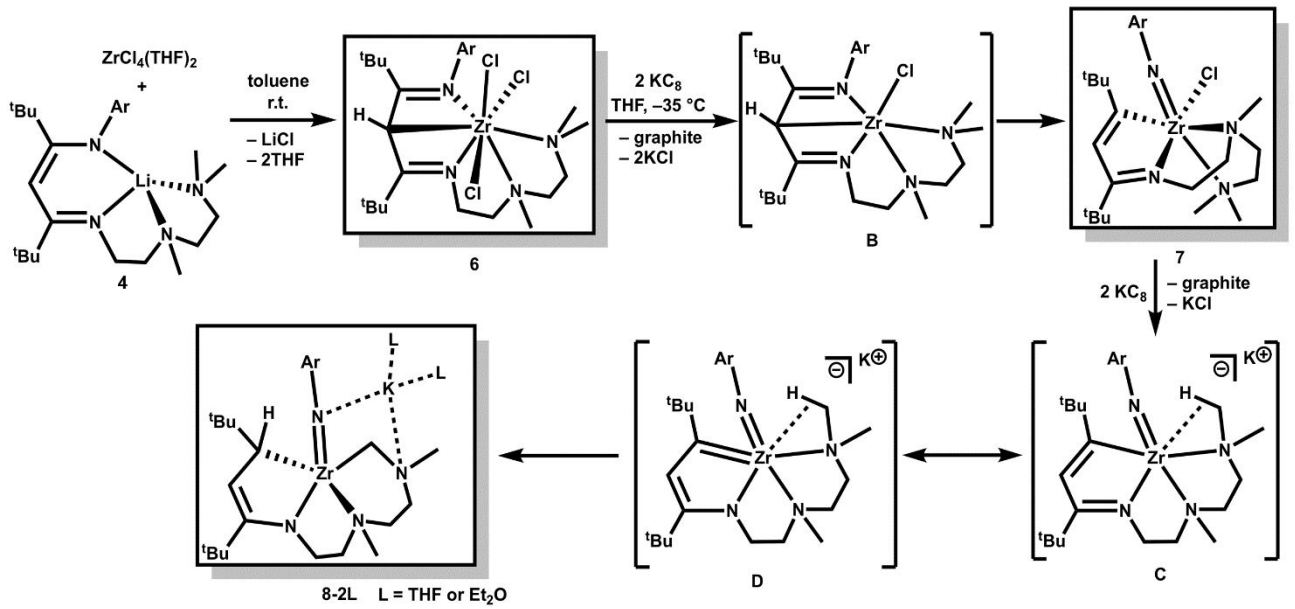


Figure 1. Solid-state structures of compounds **4** (top) and **5** (bottom) showing thermal ellipsoids at the 50% probability level.



Scheme 3. Synthesis of complex **6** with the lithio salt **4** and subsequent reductions with two equiv of KC_8 to form **7** and **8**. Plausible intermediates leading to **7** and **8** are shown in brackets.

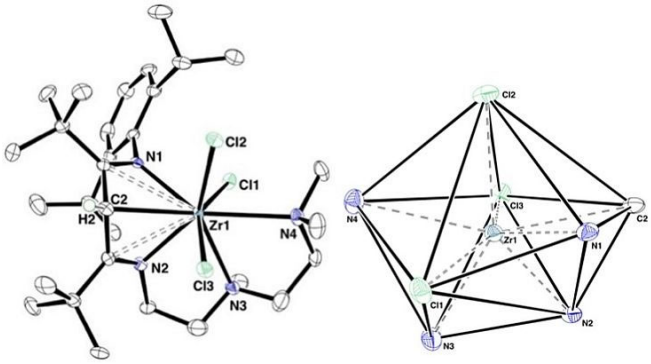


Figure 2. Solid-state structure of compound **6** (left) with H-atoms omitted for clarity with the exception of H2, and the first coordination sphere at Zr^{IV} (right) showing thermal ellipsoids at the 50% probability level.

To our surprise, however, the solid-state structure of a single crystal grown from Et_2O at −35 °C revealed an eight-coordinate Zr^{IV} complex whereby the ^{tBu}L2 not only binds through the four nitrogen sites but with coordination also occurring at the γ-C of the [NCCCN] part in the ^{tBu}L2 ligand (Figure 2). The Zr–C distance of 2.612(4) Å is comparable to those of eight-coordinated zirconium alkyl complexes.[17a,22] In contrast to **4**, the contracted C-N and elongated C–C bond distances (C–N: 1.305(5) Å, 1.337(5) Å; C–C: 1.440(6) Å, 1.418(6) Å) in the [NCCCN] skeleton exhibits bond alternation to represent a bis(imino)alkyl character of the ^{tBu}L2 ligand. As a result of this additional binding site, the [Zr(NCCCN)] ring in **6** distorts to a boat-like conformation with the metal ion and γ-C taking up the bow and stern, and with the three chloride ligands occupying a pseudo *mer*-configuration. The first coordination sphere around the zirconium center, shown in the right side of Figure 2, represents a distorted trigonal dodecahedral geometry.[23] In addition to the structural data in solid-state, the $^{13}C\{^1H\}$ NMR spectrum of **6** also showed the γ-C in the [NCCCN] framework at 78.1 ppm, which is significantly high field-shifted compared to that of the lithio salt **4** (91.9 ppm).

Reduction of **6** with two equiv of KC_8 in THF resulted in the formation of the distorted octahedral zirconium imide-chloride $[C(tBu)CHC(tBu)NCH_2CH_2N(Me)CH_2CH_2NMe_2]Zr(=NAr)(Cl)$ (**7**) isolated in 70% yield as a reddish orange solid. Salient spectroscopic features for **7** include a highly downfield $^{13}C\{^1H\}$ NMR spectroscopic resonance of the α-C in [ZrCCCN] at 248.3 ppm as well as the γ-C in the [ZrCCCN] at 187.0 ppm, which are comparable to those of reported azabutadienyl complexes.[11,17]

An XRD study of a single crystal of **7** grown from THF/pentane at −35 °C reveals mononuclear and coordinatively saturated Zr^{IV} complex with a terminal imido moiety (Zr=N, 1.8776(10) Å) (Figure 3 top and Table 1). This Zr=N bond length is comparable to those of other terminal zirconium imides reported in the literature (1.8185(17)–1.913(2) Å).[17a,24] As the result of C=N bond reductive cleavage of ^{tBu}L2, an azabutadienyl ligand chelates to the metal center, with the two pendant amino residues remaining intact. The imido ligand is *trans* to the dimethyl amino group (N1-Zr1-N4: 171.91(4)°), whereas the remaining chlorido ligand resides *transoid* to the azabutadienyl nitrogen (Cl1-Zr1-N2: 164.64(3)°). Our group[17] and others[10b,11,12,25] have observed similar C=N bond reductive cleavage reactions involving the β-diketiminato scaffold and despite having pendant amino groups, the ^{tBu}L2 ligand still succumbs to reductive cleavage of the imino group. Formation of **7** most likely traverses via a transient Zr^{II} intermediate (^{tBu}L2)ZrCl (**B**) (most likely not a concerted step and involving side-on coordination of the imine group to Zr), which readily splits the C=N bond of the ligand. It was found that another minor product was formed in the mixture when a slight excess of reductant was used. Optimization of the reaction conditions revealed that the additional material was being generated by the two-electron reduction of **7**. Accordingly, treating an isolated sample of **7** with two equiv of KC_8 in THF at −35 °C resulted in formation of the other Zr^{IV} species **8-2THF** (observed only in traces using the original conditions) which could then be isolated in 42% yield as a yellow solid (Scheme 3). Although the ^1H NMR spectrum showed the aryl imido group, the entire spectrum is quite broad and uninformative. To establish the connectivity of this new species, single crystals were grown as an Et_2O adduct, instead of the original THF adduct **8-2THF**, from a concentrated solution in Et_2O at −35 °C. Figure 3 bottom depicts the molecular structure of the ate-complex

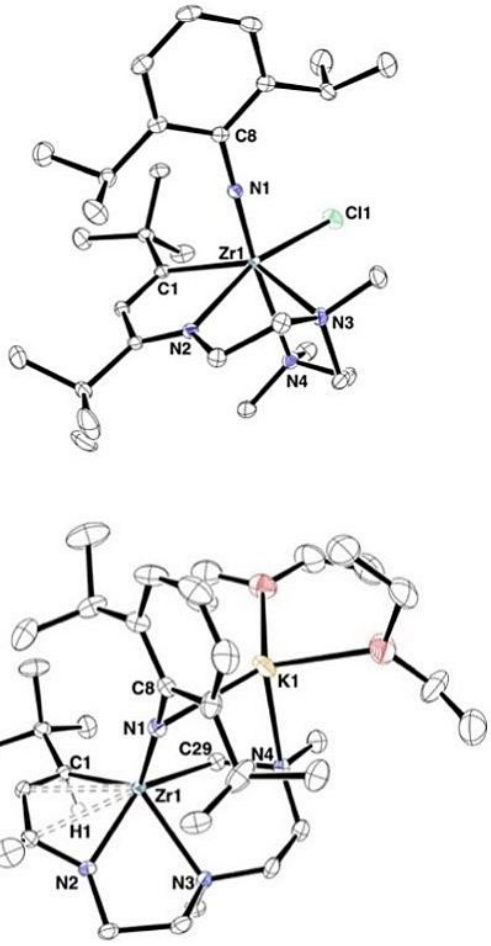


Figure 3. Solid-state structures of compounds **7** (top) and **8-2Et$_2$O** (bottom) showing thermal ellipsoids at the 50% probability level. H-atoms and co-crystallized THF have been omitted for clarity.

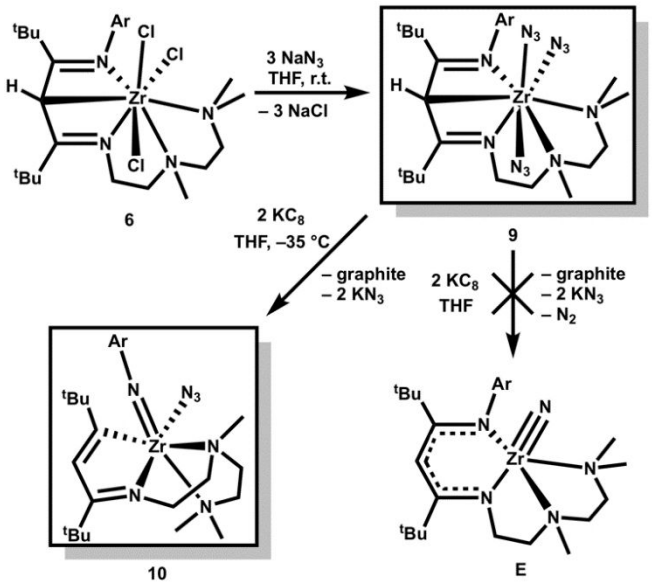
Table 1. Metric parameters in solid-state structures of compounds **6**–**10**. Bond distances (Å) and angles (°) around the Zr center.

	6 (X = Cl)	**7** (X = Cl)	**8-2Et$_2$O** (X = C29)	**9** (X = N_3)	**10** (X = N_3)
Zr-N1	2.325(3)	1.8776(10)	1.9506(15)	2.320(3)	1.881(3)
Zr-N2	2.176(4)	2.3613(10)	2.0986(15)	2.171(3)	2.349(3)
Zr-N3	2.522(3)	2.3773(11)	2.4495(15)	2.486(3)	2.378(3)
Zr-N4	2.677(4)	2.6314(11)	–	2.609(3)	2.609(3)
Zr-C1	–	2.3151(12)	2.2760(17)	–	2.321(3)
Zr-X	2.4753(11)	2.5044(4)	2.3791(18)	2.133(3)	2.186(3)
(X = Cl, N_3, C29)	2.5008(10)			2.172(3)	
	2.5608(11)			2.216(3)	
Zr out of [NC_3N] plane	1.785	–	–	1.781	–
Zr-C2	2.612(4)	–	–	2.629(3)	–
N1-Zr-N2	77.09(13)	94.74(4)	117.87(6)	76.86(10)	95.56(11)
N1-Zr-N3	128.15(12)	99.61(4)	116.36(6)	128.33(9)	96.94(11)
N1-Zr-N4	141.64(13)	171.91(4)	–	141.01(9)	169.22(11)
N2-Zr-N3	68.95(12)	71.45(4)	68.61(5)	70.62(10)	71.22(10)
N2-Zr-N4	136.60(12)	84.20(4)	–	138.93(10)	82.27(9)
N3-Zr-N4	69.60(12)	72.43(4)	–	71.07(9)	72.35(10)
X-Zr-X	84.22(4)	–	–	84.83(11)	–
(X = Cl, N_3, C29)	101.29(4)			102.01(11)	
	152.61(4)			149.90(12)	
X-Zr-C1 (X = Cl, N_3, C29)	–	113.71(3)	95.26(6)	–	114.54(11)
X-Zr-N1	75.14(9)	98.79(3)	99.96(6)	75.07(11)	101.72(12)
(X = Cl, N_3, C29)	83.33(8)			84.83(11)	
	132.24(9)			135.02(11)	
X-Zr-N2	84.15(10)	164.64(3)	136.50(6)	82.60(11)	159.71(11)
(X = Cl, N_3, C29)	106.22(10)			109.05(11)	
	140.51(9)			138.00(11)	
X-Zr-N3	78.12(9)	98.98(3)	76.05(6)	78.96(11)	95.98(11)
(X = Cl, N_3, C29)	82.42(9)			79.17(11)	
	145.69(9)			144.58(11)	
X-Zr-N4	76.80(9)	81.38(3)	–	74.63(11)	78.78(10)
(X = Cl, N_3, C29)	77.01(8)			76.23(11)	
	78.25(8)			77.27(11)	

$[K(OEt_2)_2]\{[CH(t\text{Bu})CHC(t\text{Bu})NCH_2CH_2N(Me)CH_2CH_2N(Me)CH_2]Zr{=}NAr\}$ (**8-2Et$_2$O**) (Table 1). Inspection of the structure immediately reveals that a methyl moiety of the amino group (Zr1–C29, 2.3791(18) Å), has been activated with the hydrogen being now shifted to the carbon of the formal azabutadienyl ligand in **7**. The bond distances in the five-membered framework Zr[CCCN] showed a shorter C2–C3 bond (1.391(3) Å) and longer C1–C2 (1.478(2) Å) and C3–N2 (1.388(2) Å) bonds than those of compound **7** (1.4814(18), 1.3502 (18), 1.2974(16), respectively). A potassium counter cation coordinates to the imido nitrogen (Zr1=N, 1.9506(15) Å) as well as to the β-nitrogen at the metallated site, with two Et_2O ligands completing its coordination sphere. The formation of **8-2L** (L = THF or Et_2O) from **7** and two equiv of KC_8 most likely traverses via an anionic Zr^{II} imido species (**C**) or Zr^{IV} ligand-based reduction species (**D**), which has a Zr=C double bond. Lastly, abstraction of hydrogen in a C–H bond of a methylamino group to the azametallacyclopentadienyl moiety in **D** results in the final product **8-2L**.

We recently have found that reduction of the *trans*-Zr^{IV} bis azido precursor $(PN)_2Zr(N_3)_2$ ($PN^- = N$-(2-*i*Pr_2P-4-methylphenyl)-2,4,6-trimethylanilide) with KC_8 promoted both azide elimination and N_2 extrusion to afford an unprecedented mononuclear parent imide of zirconium, namely $(PN)_2Zr{=}NH$.[26] We inquired whether replacement of all chlorido ligands for azides would circumvent the reductive C=N bond cleavage pathway for a more intuitively simpler N_2 extrusion process via 2 e^- disproportionation of N_3^- to N_2 and N^{3-}. We anticipated that reduction of the azide would expel N_2 which would require minimal reorganization energy as opposed to reductive C=N splitting via a more complex ligand rearrangement of ($^{t\text{Bu}}$L2), thus providing entry to a hypothetical neutral zirconium nitride ($^{t\text{Bu}}$L2)Zr≡N (**E**) (Scheme 4). Accordingly, treatment of complex **6** with an excess of NaN_3 in THF over 18 hours resulted in smooth formation of the tris-azido complex ($^{t\text{Bu}}$L2)$Zr(N_3)_3$ (**9**) in 88% yield as a translucent solid (Scheme 4). Although the NMR spectral data of **9** display almost identical features which were observed in the trichlorido complex **6** such as the γ-C position of [NCCCN] at 77.2 ppm, the IR spectrum revealed a diagnostic ν(N_3) stretch at 2099 cm^{-1} as a very strong stretch similar to reported zirconium azides[27] and other early-transition metal tris-azido complexes.[28] An XRD of **9** confirmed the presence of three azido ligands bound to Zr^{IV} ($Zr\text{-}N_{azide}$, 2.133(3)-2.216(3) Å) and with an overall similar trigonal dodecahedral geometry[23] to the chloride precursor **6** (Figure 4, left and Table 1).

With the azido ligands in place, we then subjected complex **9** to reducing conditions akin to how complex **6** was treated with KC_8. Accordingly, adding two equiv of KC_8 to **9** in THF at −35 °C, and allowing the mixture to stir for 2 hours at room temperature resulted in formation of the azide-imide $[C(t\text{Bu})CHC(t\text{Bu})NCH_2CH_2N(Me)CH_2CH_2NMe_2]Zr{=}$



Scheme 4. Synthesis of complex **9** from salt metathesis of **6** and NaN_3 as well as subsequent two electron reduction to **10**. Formation of a hypothetical zirconium nitride **E** via reduction of **9** was not observed.

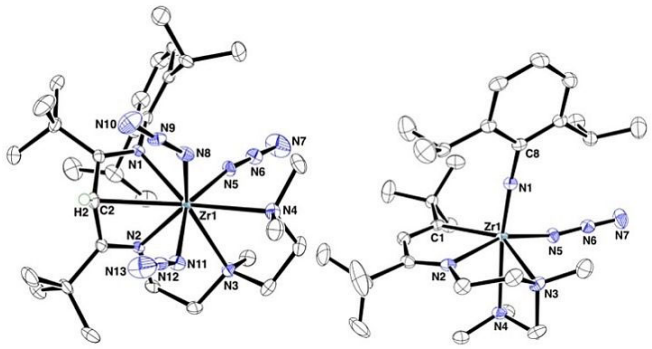


Figure 4. Solid-state structures of compounds **9** (left) and **10** (right) showing thermal ellipsoids at the 50% probability level. H-atoms and co-crystallized THF have been omitted for clarity.

$NAr(N_3)$ (**10**) isolated in 51% yield as a red solid (Scheme 4). Disappointingly, we observe no evidence for the formation of the nitride **E**, therefore implying that azide disproportionation of the intermediate the Zr^{II} (^{tBu}L2)Zr(N_3) to N_2 and N^{3-} is unfavourable with respect to C=N bond cleavage of the ^{tBu}L2, at least under our reaction conditions. Formation of **10** is based on ^{1}H and ^{13}C NMR spectroscopic data, which resemble the chlorido analogue **7** (vide supra), as well as an IR stretch ($\nu(N_3)$: 2019 cm^{-1}). In addition, an XRD study on a single crystal of **10** confirmed the monomeric and pseudo octahedral nature of the Zr center, the terminal imido group (Zr=N, 1.881(3) Å) and the reductive cleavage of the C=N bond on ^{tBu}L2 (Figure 4, right and Table 1).

Conclusions

We have shown a synthetic route to the lithio salt of a multidentate β-diketiminato ligand having pendant amino groups, Li(^{tBu}L2) (**4**). Using the lithio salt **4**, eight-coordinated complexes of zirconium with three chlorido and azido ligands have been prepared and structurally characterized. Reduction of these zirconium(IV) complexes **6** and **9** with KC_8 resulted in formation of azabutadienyl-imido complexes **7** and **10** via degradation of the β-diketiminato scaffold by a low-valent zirconium species. Further reduction of the azabutadienyl-imide **7** by KC_8 formed an anionic imido species **8-2L**, which has also been structurally characterized. Syntheses of other metal complexes and further reactivity studies of the zirconium complexes will be forthcoming.

Experimental Section

General Procedure.

All operations were performed in an M. Braun glove box or using Schlenk techniques under a nitrogen atmosphere unless otherwise stated. Anhydrous hydrocarbon solvents and CH_2Cl_2 were purchased from Fisher Scientific. Stabilizer-free ethereal solvents (Et_2O and THF) were purchased from Alfa Aesar. All anhydrous hydrocarbon solvents (pentane, hexane and toluene) were purified and dried by passage through two columns of activated alumina and Q-5 drying agent in a Grubbs-type solvent system. CH_2Cl_2 and ethereal solvents were dried by passage through two columns of activated alumina. All bulk solvents were kept over 4 Å molecular sieves and sodium with the exception of CH_2Cl_2. Benzene-d_6 (Cambridge Isotope Laboratories) was dried and degassed over a potassium mirror prior to use. Chloroform-*d* (Cambridge Isotope Laboratories) was dried and distilled over calcium hydride prior to use. Celite and 4 Å molecular sieves were activated under vacuum overnight at 200 °C. $ZrCl_4(THF)_2$,[29] KC_8,[30] *N*^{1}-(2-aminoethyl)-*N*^{1},*N*^{2},*N*^{2}-trimethylethane-1,2-diamine (**1**),[18] and 1-chloro-2-(2,6-diisopropylphenylimino)-2,2-dimethylpropane[31] were prepared according to the reported procedures. NaN_3 was dried by stirring in anhydrous THF overnight, washed with anhydrous Et_2O and pentane and then evacuated at room temperature overnight. All other chemicals were purchased from commercial sources and used as received. ^{1}H, ^{13}C, ^{7}Li and 2D (COSY, HSQC, and HMBC) NMR spectra were recorded on a Bruker AV-II 500 MHz or AV-III 400 MHz spectrometer. ^{1}H and ^{13}C{^{1}H} NMR chemical shifts are reported referenced to the internal residual proton or carbon resonances of C_6D_6 (δ = 7.16 ppm or 128.06 ppm) or $CDCl_3$ (δ = 7.26 ppm or 77.16 ppm). ^{7}Li NMR chemical shift is reported referenced to the external LiCl solution in D_2O (δ = 0.00 ppm). IR samples were prepared by a KBr plate method (JASCO Tablet Master) and IR spectra were obtained on a JASCO FT/IR-4600 spectrometer. Elemental analyses were performed by Midwest Microlab, Inc (Indiana, USA).

Synthesis of compound 2.

To a colorless solution of 3,3-dimehyl-2-butanone (3.12 g, 31.2 mmol) and **1** (4.28 g, 29.5 mmol) in toluene (100 mL) was added *p*-toluenesulfonic acid monohydrate (500 mg, 2.63 mmol) as a solid at room temperature. The reaction mixture was heated at 120 °C under a dry nitrogen atmosphere equipped with a Dean–Stark apparatus and a Vigreux column. During condensation, the reaction mixture gradually changed in color to brown and water (ca. 0.5 mL) was collected in the Dean–Stark apparatus. After refluxing for 18 hours, the reaction mixture was cooled down to room temperature. The solvent was removed under vacuum at room temperature to yield a brown oil. From the brown oil, a colorless oil of pure *N*^{1}-(2-((3,3-dimethylbutan-2-ylidene)amino)ethyl)-*N*^{1},*N*^{2},*N*^{2}-trimethylethane-1,2-diamine **2** (4.73 g, 20.8 mmol, 71% yield) was obtained by distillation (200 mTorr at 80–85 °C).

^{1}H NMR (500 MHz, Benzene-d_6, 300 K): δ = 3.36 (t, $^3J_{HH}$ = 8 Hz, 2H, NCH_2CH$_2$N), 2.83 (t, $^3J_{HH}$ = 8 Hz, 2H, NCH_2CH$_2$N), 2.59 (t, $^3J_{HH}$ = 8 Hz, 2H, NCH_2CH$_2$N), 2.41 (t, $^3J_{HH}$ = 8 Hz, 2H, NCH_2CH$_2$N), 2.28 (s, 3H, NMe), 2.13 (s, 6H, NMe_2), 1.48 (s, 3H, N=C-Me), 1.11 ppm (s, 9H, N=C-*t*Bu). ^{1}H NMR (400 MHz, Chloroform-*d*, 300 K): δ = 3.35 (t, $^3J_{HH}$ = 8 Hz, 2H, NCH_2CH$_2$N), 2.64 (t, $^3J_{HH}$ = 8 Hz, 2H, NCH_2CH$_2$N), 2.55 (t, $^3J_{HH}$ = 8 Hz, 2H, NCH_2CH$_2$N), 2.41 (t, $^3J_{HH}$ = 8 Hz, 2H, NCH_2CH$_2$N), 2.31 (s, 3H, NMe), 2.22 (s, 6H, NMe_2), 1.77 (s, 3H, N=C-Me), 1.07 ppm (s, 9H, N=C-*t*Bu). ^{13}C{^{1}H} NMR (126 MHz, Benzene-d_6, 300 K): δ = 173.78 (N=*C*), 59.75 (NCH$_2$CH$_2$N), 58.50 (NCH$_2$CH$_2$N), 57.13 (NCH$_2$CH$_2$N), 50.79 (NCH$_2$CH$_2$N), 46.11 (N (CH_3)$_2$), 43.54 (NCH_3), 40.61 (N=C–*C*(CH_3)$_3$), 28.00 (N=C–C(CH_3)$_3$), 12.75 ppm (N=C-CH_3). IR (KBr): $\tilde{\nu}$ = 2965 (s), 2901 (s), 2864 (s), 2765 (s), 1654 (s), 1462 (s), 1362 (m), 1130 (m), 1029 (m), 935 (w), 846 (w), 827 (w), 790 (w), 467 (w), 412 cm^{-1} (w). Anal. Calcd. for $C_{13}H_{29}N_3$: C, 68.67; H, 12.86; N, 18.48. Found: C, 68.57; H, 12.98; N, 18.33.

Synthesis of compound 3.

Under a dry nitrogen atmosphere, a clear solution of **2** (2.00 g, 8.80 mmol) in THF (40 mL) was cooled at −78 °C. Li*n*Bu (2.5 M in hexane, 3.55 mL, 8.88 mmol) was added via a syringe into the THF solution of **2** dropwise. After addition of Li*n*Bu, the reaction mix-

ture was allowed to warm up to room temperature, resulting in a color change to pale yellow. After stirred at room temperature for 2 hours, the pale yellow solution was transferred via a cannula into 1-chloro-2-(2,6-diisopropylphenylimino)-2,2-dimethylpropane (2.47 g, 8.83 mmol) diluted in THF (30 mL) cooled at −78 °C, resulting in a color change to yellowish orange and precipitation of a white solid (LiCl). The reaction mixture was warmed up to room temperature. After stirred at room temperature for 1 hour, all volatile materials were removed under vacuum. The orange waxy residue was dissolved in hexane (50 mL) and filtered through Celite to remove LiCl. The filtrate was concentrated to ca. 10 mL and a yellow solid was precipitated. The precipitated yellow solid was collected by filtration and dried under vacuum. The obtained yellow solid was confirmed as the lithio salt **4** (1.87 g, 3.92 mmol, 45% yield) by NMR spectroscopy and X-ray crystallography. The filtrate part was evaporated under vacuum and the crude product **3** (Figure S4) was obtained as an orange oil (1.11 g, 2.35 mmol calculated as **3**, 27% crude yield). Purification of **3** from the obtained oil by distillation or column chromatography was failed.

Synthesis of compound 4.

Route A: To a yellowish orange solution of crude **3** (1.00 g, 2.10 mmol calculated as **3**) in hexane (20 mL) was added L*in*Bu (2.5 M in hexane, 0.85 mL, 2.13 mmol) dropwise at −35 °C. The reaction mixture was warmed up to room temperature, resulting in a small amount of a white powder. After stirred at room temperature for 1 hour, the yellowish orange reaction mixture was filtered through Celite to remove insoluble materials. The filtrate was dried under vacuum. The brown residue was suspended in pentane (10 mL) and a yellow solid was formed. The yellow solid was collected by filtration and dried under vacuum to yield pure compound **4** (394 mg, 826 μmol, ca. 39% yield based on crude **3**). The brown filtrate from this synthesis was cooled at −35 °C overnight. A few translucent crystals were grown and confirmed as compound **5** by X-ray crystallography.

Method B: Under a dry nitrogen atmosphere, a colorless solution of **2** (6.00 g, 26.4 mmol) in THF (80 mL) was cooled at −78 °C. L*in*Bu (2.5 M in hexane, 10.8 mL, 27.0 mmol) was added via a syringe into the THF solution of **2** dropwise and the reaction mixture was at room temperature for 2 hours. The pale yellow solution was transferred via a cannula into 1-chloro-2-(2,6-diisopropylphenylimino)-2,2-dimethylpropane (7.45 g, 26.6 mmol) in THF (50 mL) cooled at −78 °C. The reaction mixture was warmed up to room temperature and stirred for 1 hour. All volatile materials were removed under vacuum. The orange residue was dissolved in hexane (100 mL) and filtered through Celite. THF (10 mL) was added into the filtrate. The mixture was cooled at −78 °C and L*in*Bu (2.5 M in hexane, 10.5 mL, 26.3 mmol) was added dropwise. After addition of L*in*Bu, the mixture was stirred at room temperature for 1 hour. The orange mixture was filtered through Celite and the filtrate was dried under vacuum. The yellowish orange residue was suspended in pentane (20 mL). A yellow solid was collected by filtration, washed with pentane (10 mL × 2) and dried under vacuum to give compound **4** (6.12 g, 12.8 mmol, 48% yield from **2**). Single crystals suitable for an XRD study were obtained from a concentrated solution in pentane at −35 °C.

^{1}H NMR (400 MHz, Benzene-d_6, 300 K): δ = 7.16 (overlapped with C_6D_5H, 2H, Ar-*H*), 7.02 (t, $^3J_{HH}$ = 8 Hz, 1H, Ar-*H*), 5.32 (s, 1H, NC(*t*Bu)C*H*C(*t*Bu)N), 3.65–3.53 (m, overlapped, 3H, ArC*H*Me$_2$ and NC*H*$_2$), 3.46 (m, 1H, ArC*H*Me$_2$), 2.34 (m, 2H, NC*H*$_2$), 1.93 (s, 6H, N*Me*$_2$), 1.95–1.90 (m, overlapped, 2H, NC*H*$_2$), 1.71 (s, 3H, N*Me*), 1.72–1.60 (m, overlapped, 1H, NC*H*$_2$), 1.45 (br, 6H, ArCH*Me*$_2$), 1.47–1.41 (m, overlapped, 1H, NC*H*$_2$), 1.39 (s, 9H, *t*Bu), 1.34 (s, 9H, *t*Bu), 1.20 (d, 3H, $^3J_{HH}$ = 6 Hz, ArCH*Me*$_2$), 1.16 ppm (d, 3H, $^3J_{HH}$ = 6 Hz, ArCH*Me*$_2$). ^{13}C{^{1}H} NMR (101 MHz, Benzene-d_6, 300 K): δ = 172.14 (*C*tBu), 171.12 (*C*tBu), 151.60 (Ar), 140.81 (Ar), 138.54 (Ar), 122.82 (Ar), 122.65 (Ar), 119.52 (Ar), 91.89 (NC(*t*Bu)CHC(*t*Bu)N), 60.68 (NCH$_2$CH$_2$N), 58.03 (NCH$_2$CH$_2$N), 51.07 (NCH$_2$CH$_2$N), 46.76 (NCH$_2$CH$_2$N), 45.66 (N(CH$_3$)$_2$), 44.99 (NCH$_3$), 44.17 (*C*(CH$_3$)$_3$), 40.05 (*C*(CH$_3$)$_3$), 33.39 (C(*C*H$_3$)$_3$), 30.62 (C(*C*H$_3$)$_3$), 27.83 (Ar-CH(*C*H$_3$)$_2$), 25.98 (Ar-CH(*C*H$_3$)$_2$), 23.59 (Ar-*C*H(CH$_3$)$_2$), 22.21 ppm (Ar-CH(*C*H$_3$)$_2$). ^{7}Li NMR (155 MHz, Benzene-d_6, 300 K): δ = 1.73 ppm (s). IR (KBr): $\tilde{\nu}$ = 3141 (m), 3050 (s), 2953 (s), 2863 (s), 2786 (s), 2499 (s), 1561 (s), 1491 (s), 1455 (br), 1400 (br), 1361 (s), 1330 (s), 1286 (s), 1269 (m), 1255 (m), 1213 (m), 1183 (m), 1164 (m), 1141 (m), 1119 (m), 1102 (m), 1065 (m), 1038 (m), 1020 (m), 986 (w), 933 (w), 903 (w), 884 (m), 831 (m), 805 (w), 774 (s), 756 (s), 711 (s), 688 (s), 657 (w), 628 (w), 585 (w), 527 (w), 498 (w), 453 (w), 430 (w), 414 (w), 402 cm^{-1} (w). Anal. Calcd. for $C_{30}H_{53}N_4Li$: C, 75.58; H, 11.21; N, 11.75. Found: C, 75.72; H, 11.29; N, 11.61.

Synthesis of compound 6.

To a white suspension of $ZrCl_4(THF)_2$ (633 mg, 1.68 mmol) in toluene (30 mL) was added **4** (800 mg, 1.68 mmol) as solid at room temperature. The reaction mixture gradually changed in color from yellow to pale yellow. After stirred at room temperature for 3 hours, all volatile materials were removed under vacuum. The pale yellow residue was suspended in CH_2Cl_2 (30 mL) and filtered through Celite to remove insoluble materials. The pale yellow filtrate was dried under vacuum. The residue was suspended in pentane (10 mL) and the pale yellow solid was collected by filtration, washed with pentane (5 mL) and dried under vacuum to yield compound **6** (947 mg, 1.42 mmol, 85% yield). Single crystals suitable for an XRD study were obtained from a concentrated solution in Et_2O at −35 °C.

^{1}H NMR (400 MHz, Chloroform-*d*, 300 K): δ = 7.11 (d, $^3J_{HH}$ = 6 Hz, 2H, Ar-*H*), 6.95 (br, 1H, Ar-*H*), 5.38 (s, 1H, NC(*t*Bu)C*H*C(*t*Bu)N), 4.41 (br, 1H, NC*H*$_2$), 4.13 (br, 3H, NC*H*$_2$ and 2 *x* ArC*H*Me$_2$), 3.85 (br, 1H, NC*H*$_2$), 3.34 (br, 1H, NC*H*$_2$), 2.78 (s, 6H, N*Me*$_2$), 2.75 (N*Me*), 2.61 (br, 1H, NC*H*$_2$), 2.36–2.10 (br, 3H, NC*H*$_2$), 1.53 (s, 9H, *t*Bu), 1.36 (br, 3H, ArCH*Me*$_2$), 1.26 (br, 3H, ArCH*Me*$_2$), 1.15 (s, 9H, *t*Bu), 1.11 (br, 3H, ArCH*Me*$_2$), 1.00 ppm (br, 3H, ArCH*Me*$_2$). ^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*, 300 K): δ = 173.08 (*C*tBu), 166.37 (*C*tBu), 146.16 (Ar), 144.27 (Ar), 141.29 (Ar), 125.84 (Ar), 124.23 (Ar), 122.21 (Ar), 78.12 (NC(*t*Bu)CHC(*t*Bu)N), 63.38 (NCH$_2$CH$_2$N), 59.35 (NCH$_2$CH$_2$N), 58.95 (NCH$_2$CH$_2$N), 52.14 (N(CH$_3$)$_2$), 50.52 (NCH$_2$CH$_2$N), 49.83 (NCH$_3$), 43.56 (*C*(CH$_3$)$_3$), 40.40 (*C*(CH$_3$)$_3$), 30.83 (C(*C*H$_3$)$_3$), 29.64 (C(*C*H$_3$)$_3$), 28.20 (Ar-CH(*C*H$_3$)$_2$), 27.32 (Ar-CH(*C*H$_3$)$_2$), 25.98 (2 *x* Ar-CH(*C*H$_3$)$_2$), 24.82 (Ar-*C*H(CH$_3$)$_2$), 23.42 (Ar-CH(*C*H$_3$)$_2$). IR (KBr): $\tilde{\nu}$ = 2962 (s), 2867 (m), 1646 (w), 1558 (w), 1466 (s), 1387 (m), 1363 (m), 1326 (m), 1204 (m), 1042 (m), 933 (m), 784 (m), 761 (m), 623 (w), 517 (w), 432 cm^{-1} (w). Anal. Calcd. for $C_{30}H_{53}N_4Cl_3Zr$: C, 53.99; H, 8.01; N, 8.40. Found: C, 53.79; H, 8.13; N, 8.22.

Synthesis of compound 7.

To a pale yellow solution of **6** (200 mg, 300 μmol) in THF (5 mL) was added KC_8 (86.1 mg, 637 μmol) in THF (5 mL) at −35 °C. The reaction mixture was stirred at room temperature for 2 hours and filtered through Celite to remove insoluble materials. The reddish orange filtrate was concentrated to ca. 5 mL, layered with pentane (5 mL) and stored at −35 °C to afford compound **7**·0.5(THF) (133 mg, 210 μmol, 70% yield) as an orange crystalline solid. The amount of the residual THF molecule in the obtained solid was determined by ^{1}H NMR spectroscopy and elemental analysis. Single

crystals suitable for an XRD study were obtained from a layered solution in THF with pentane at −35 °C.

^{1}H NMR (400 MHz, Benzene-d_6, 300 K): δ = 7.25 (d, $^3J_{HH}$ = 7 Hz, 2H, Ar-*H*), 6.96 (t, $^3J_{HH}$ = 7 Hz, 1H, Ar-*H*), 6.92 (s, 1H, ZrC(*t*Bu)C*H*C(*t*Bu)N), 4.73 (br, 2H, ArC*H*Me$_2$), 3.58 (br, 2H, 0.5 THF), 3.52–3.47 (m, 1H, NC*H*$_2$), 3.56–3.21 (m, overlapped, 2H, NC*H*$_2$), 2.96 (br t, 1H, NC*H*$_2$), 2.49 (br s, 6H, N*Me*$_2$), 2.46 (s, 3H, N*Me*), 2.11 (br t, 1H, NC*H*$_2$), 1.64 (br, 2H, 0.5 THF), 1.56 (d, $^3J_{HH}$ = 7 Hz, 6H, ArCH*Me*$_2$), 1.49 (d, $^3J_{HH}$ = 6 Hz, 6H, ArCH*Me*$_2$), 1.39 (s, 9H, *t*Bu), 1.43–1.39 (m, overlapped, 1H, NC*H*$_2$), 1.22 (br t, 2H, NC*H*$_2$), 1.10 ppm (s, 9H, *t*Bu). ^{13}C{^{1}H} NMR (101 MHz, Benzene-d_6/THF, 300 K): δ = 248.29 (Zr*C*tBu), 187.04 (NC*t*Bu), 173.06 (Ar), 152.87 (Ar), 144.28 (Ar), 129.82 (Ar), 125.98 (Ar), 122.06 (Ar), 117.22 (C(*t*Bu)CHC(*t*Bu)N), 59.24 (NCH$_2$CH$_2$N), 56.94 (NCH$_2$CH$_2$N), 52.31 (NCH$_2$CH$_2$N), 48.29 (NCH$_2$CH$_2$N), 47.46 (N(CH$_3$)$_2$), 43.53 (NCH$_3$), 40.82 (*C*(CH$_3$)$_3$), 40.34 (*C*(CH$_3$)$_3$), 31.17 (C(CH$_3$)$_3$), 30.93 (C(CH$_3$)$_3$), 26.98 (Ar-CH(CH$_3$)$_2$), 25.90 (Ar-CH(CH$_3$)$_2$), 25.11 (Ar-CH(CH$_3$)$_2$), 24.60 ppm (Ar-CH(CH$_3$)$_2$). IR (KBr): $\tilde{\nu}$ = 2956 (s), 2864 (s), 1625 (w), 1582 (w), 1540 (w), 1464 (s), 1420 (s), 1398 (w), 1340 (w), 1324 (s), 1284 (s), 1237 (m), 1204 (m), 1127 (m), 1101 (m), 1077 (m), 1065 (m), 1025 (m), 1006 (m), 984 (m), 949 (m), 930 (m), 893 (m), 861 (m), 802 (m), 785 (s), 761 (s), 684 (w), 632 (w), 550 (w), 517 cm^{-1} (w). Anal. Calcd. for $C_{32}H_{57}N_4O_{0.5}ClZr$: C, 60.77; H, 9.08; N, 8.86. Found: C, 60.87; H, 9.29; N, 8.75.

Synthesis of compound 8-2THF.

To an orange solution of **7**·0.5(THF) (100 mg, 158 μmol) in THF (10 mL) was added KC_8 (48.1 mg, 356 μmol) in THF (5 mL) at −35 °C. The reaction mixture was stirred at room temperature for 2 hours and filtered through Celite to remove insoluble materials. The dark brown filtrate was concentrated to ca. 1 mL, layered with pentane (5 mL) and stored at −35 °C to afford compound **8-2THF** (49.3 mg, 826 μmol, 42% yield) as yellow crystals. Single crystals suitable for an XRD study were obtained from a concentrated solution in Et$_2$O at −35 °C as an Et$_2$O adduct **8-2Et$_2$O**.

^{1}H NMR (400 MHz, Benzene-d_6, 300 K): δ = 7.09 (d, $^3J_{HH}$ = 6 Hz, 2H, Ar-*H*), 6.69 (t, $^3J_{HH}$ = 6 Hz, 1H, Ar-*H*), 4.82 (br, 1H, C(*t*Bu)C*H*C(*t*Bu)N), 4.30–3.70 (br, overlapped, 5H, ArC*H*Me$_2$ and NC*H*$_2$), 3.56 (br, THF), 3.31 (br, 1H, NC*H*$_2$), 2.56 (br, 1H, NC*H*$_2$), 2.25–1.90 (br, overlapped, 4H, N*Me* and NC*H*$_2$), 1.84 (br, 3H, N*Me*), 1.50 (br, 6H, ArCH*Me*$_2$), 1.40 (br, THF), 1.35 (br, 6H, ArCH*Me*$_2$), 1.31 (br s, 18H, *t*Bu), 1.30–1.20 (overlapped, 4H, NC*H*$_2$ and ZrC*H*$_2$N), 0.56 ppm (br, 1H, ZrCH). Poor solubility and fluxional behavior of **8-2THF** in solution prevent us from acquiring the ^{13}C NMR and VT-NMR spectra. IR (KBr): $\tilde{\nu}$ = 2954 (s), 2865 (s), 2807 (w), 2700 (w), 1637 (br), 1579 (s), 1525 (w), 1459 (s), 1407 (s), 1354 (s), 1343 (s), 1282 (s), 1259 (w), 1237 (w), 1209 (w), 1172 (w), 1136 (w), 1109 (w), 1068 (w), 1050 (w), 1016 (w), 969 (w), 916 (m), 846 (w), 777 (w), 752 (m), 712 (w), 637 (w), 602 (w), 573 (w), 512 (w), 458 (w), 446 cm^{-1} (w). Anal. Calcd. for $C_{38}H_{69}N_4O_2KZr$: C, 61.32; H, 9.34; N, 7.53. Found: C, 60.91; H, 9.14; N, 7.61. The elemental analysis data shows a low carbon value probably due to incomplete combustion.

Synthesis of compound 9.

To a pale yellow solution of **6** (160 mg, 240 μmol) in THF (10 mL) was added NaN_3 (84.1 mg, 1.29 mmol) in THF (5 mL) at room temperature. The reaction mixture was stirred at room temperature for 18 hours, resulting in a color change from pale yellow to colorless. The reaction mixture was filtered through Celite. The colorless filtrate was concentrated to ca. 1 mL, layered with pentane (5 mL) and stored at −35 °C to afford compound **9** (146 mg, 212 μmol, 88% yield) as a translucent crystalline solid. Single crystals suitable for an XRD study were obtained from a layered solution in THF with pentane at −35 °C.

^{1}H NMR (400 MHz, Benzene-d_6, 300 K): δ = 7.16 (overlapped with C_6D_5H, 2H, Ar-*H*), 7.03 (t, $^3J_{HH}$ = 7 Hz, 1H, Ar-*H*), 5.53 (s, 1H, NC(*t*Bu)C*H*C(*t*Bu)N), 3.98 (br, 1H ArC*H*Me$_2$), 3.70 (m, 1H, NC*H*$_2$), 3.48 (br t, 1H, NC*H*$_2$), 3.11 (br t, 1H, NC*H*$_2$), 2.63 (br t, 1H, NC*H*$_2$), 2.33 (br, 1H ArC*H*Me$_2$), 2.30–2.25 (overlapped, m, 2H, NC*H*$_2$), 2.28 (s, 6H, N*Me*$_2$), 2.08 (N*Me*), 1.61 (overlapped, m, 1H, NC*H*$_2$), 1.62 (br, 3H, ArCH*Me*$_2$), 1.52 (br, 3H, ArCH*Me*$_2$), 1.33 (s, 9H, *t*Bu), 1.30–1.28 (overlapped, m, 1H, NC*H*$_2$), 1.16 (br, 3H, ArCH*Me*$_2$), 0.97 ppm (br, 3H, ArCH*Me*$_2$). ^{13}C{^{1}H} NMR (101 MHz, Benzene-d_6/THF, 300 K): δ = 174.80 (*C*tBu), 166.62 (*C*tBu), 145.71 (Ar), 142.63 (Ar), 140.62 (Ar), 126.49 (Ar), 124.88 (Ar), 123.20 (Ar), 77.21 (NC(*t*Bu)CHC(*t*Bu)N), 65.25 (NCH$_2$CH$_2$N), 59.01 (NCH$_2$CH$_2$N), 58.24 (NCH$_2$CH$_2$N), 49.94 (N(CH$_3$)$_2$), 45.39 (NCH$_2$CH$_2$N), 43.67 (NCH$_3$), 43.67 (*C*(CH$_3$)$_3$), 40.17 (*C*(CH$_3$)$_3$), 31.19 (C(CH$_3$)$_3$), 29.56 (C(CH$_3$)$_3$), 28.41 (Ar-CH(CH$_3$)$_2$), 27.68 (Ar-CH(CH$_3$)$_2$), 25.74 (Ar-CH(CH$_3$)$_2$), 25.39 (Ar-CH(CH$_3$)$_2$), 25.05 (Ar-CH(CH$_3$)$_2$), 23.51 ppm (Ar-CH(CH$_3$)$_2$). IR (KBr): $\tilde{\nu}$ = 3059 (m), 3025 (s), 2968 (s), 2926 (s), 2870 (s), 2099 (s), 1543 (br), 1466 (s), 1392 (s), 1349 (m), 1329 (m), 1285 (m), 1256 (w), 1237 (w), 1203 (m), 1176 (m), 1164 (m), 1141 (m), 1129 (m), 1102 (m), 1078 (m), 1063 (m), 1049 (m), 1029 (m), 1008 (m), 961 (m), 935 (m), 911 (w), 892 (w), 847 (w), 805 (w), 785 (s), 770 (w), 738 (w), 696 (w), 624 (w), 601 (w), 590 (w), 576 (w), 506 (w), 494 cm^{-1} (w). Anal. Calcd. for $C_{30}H_{53}N_{13}Zr$: C, 52.44; H, 7.78; N, 26.50. Found: C, 52.56; H, 7.91; N, 26.21.

Synthesis of compound 10.

To a white suspension of **9** (300 mg, 437 μmol) in THF (10 mL) was added KC_8 (65.1 mg, 482 μmol) in THF (5 mL) at −35 °C. The reaction mixture was stirred at room temperature for 2 hours and filtered through Celite to remove insoluble materials. The reddish orange filtrate was concentrated to ca. 5 mL, layered with pentane (5 mL) and stored at −35 °C to afford compound **10**·THF (151 mg, 224 μmol, 51% yield) as an orange crystalline solid. The amount of the residual THF molecule in the obtained solid was determined by ^{1}H NMR spectroscopy and elemental analysis. Single crystals suitable for an XRD study were obtained from a concentrated solution in THF at −35 °C.

^{1}H NMR (400 MHz, Benzene-d_6, 300 K): δ = 7.24 (d, $^3J_{HH}$ = 7 Hz, 2H, Ar-*H*), 6.93 (t, $^3J_{HH}$ = 7 Hz, 1H, Ar-*H*), 6.88 (s, 1H, ZrC(*t*Bu)C*H*C(*t*Bu)N), 4.52 (br, 2H, ArC*H*Me$_2$), 3.58 (br, 4H, THF), 3.48–3.44 (m, 1H, NC*H*$_2$), 3.33–3.12 (m, overlapped, 2H, NC*H*$_2$), 2.47 (br t, 1H, NC*H*$_2$), 2.28 (br s, 6H, N*Me*$_2$), 2.19 (s, 3H, N*Me*), 2.01 (br t, 1H, NC*H*$_2$), 1.60 (br, 2H, 0.5 THF), 1.65–1.60 (overlapped, 1H, NC*H*$_2$), 1.53 (br, 6H, ArCH*Me*$_2$), 1.42 (br, 6H, ArCH*Me*$_2$), 1.31 (s, 9H, *t*Bu), 1.18 (br d, 2H, NC*H*$_2$), 1.10 ppm (s, 9H, *t*Bu). ^{13}C{^{1}H} NMR (101 MHz, Benzene-d_6/THF, 300 K): δ = 152.89 (Ar), 143.70 (Ar), 130.10 (Ar), 121.68 (Ar), 116.83 (C(*t*Bu)CHC(*t*Bu)N), 61.61 (NCH$_2$CH$_2$N), 59.30 (NCH$_2$CH$_2$N), 57.30 (NCH$_2$CH$_2$N), 52.24 (NCH$_2$CH$_2$N), 48.19 (N(CH$_3$)$_2$), 46.27 (NCH$_3$), 41.35 (*C*(CH$_3$)$_3$), 41.08 (*C*(CH$_3$)$_3$), 31.01 (C(CH$_3$)$_3$), 29.81 (C(CH$_3$)$_3$), 27.33 (Ar-CH(CH$_3$)$_2$), 25.76 (Ar-CH(CH$_3$)$_2$), 24.52 (Ar-CH(CH$_3$)$_2$), 24.44 ppm (Ar-CH(CH$_3$)$_2$). Two resonances of the [*C*(*t*Bu)] groups could not be located due to poor solubility of the compound. IR (KBr): $\tilde{\nu}$ = 3040 (m), 2956 (s), 2861 (s), 2091 (s), 1581 (m), 1459 (s), 1417 (s), 1363 (s), 1334 (s), 1282 (s), 1258 (m), 1204 (w), 1175 (w), 1128 (w), 1105 (w), 1084, 1065 (s), 1022 (w), 1000 (w), 965 (w), 944 (m), 930 (w), 893 (w), 857 (w), 781 (s), 748 (s), 718 (w), 656 (w), 601 (w), 551 (w), 512 (w), 481 (w), 456 cm^{-1} (w). Anal. Calcd. for $C_{34}H_{61}N_7OZr$: C, 60.49; H, 9.11; N, 14.52. Found: C, 60.31; H, 9.19; N, 14.66.

Crystallographic studies.

Crystallographic data (CCDC 1898832–1898838) are summarized in Table S1–S7. Suitable crystals for X-ray analyses were placed on the end of a Cryoloop coated in NVH oil. The X-ray intensity data collection was carried out on a Bruker APEXII CCD area detector for **4**, **5**, **6**, **7**, and **8-2Et$_2$O** and a Bruker D8QUEST CMOS area detector for **9** and **10** using graphite-monochromated $Mo_{K\alpha}$ radiation ($\lambda =$ 0.71073 Å) at 100(2) K. Preliminary indexing was performed from a series of twenty-four for **4**, **5**, **6**, **7**, and **8-2Et$_2$O**, or thirty-six for **9** and **10**, 0.5° rotation frames with exposures of 10 seconds. Rotation frames were integrated using SAINT,[32] producing a listing of non-averaged F^2 and $\sigma(F^2)$ values. The intensity data were corrected for Lorentz and polarization effects and for absorption using SADABS.[33] The initial structure was determined by the direct method on SHELXS.[34] The further structure determination was performed by Fourier transform method and refined by least squares method on SHELXL.[34] All reflections were used during refinement. Non-hydrogen atoms were refined anisotropically and hydrogen atoms were refined using riding models. For **4**, the amino-ethylene group was disordered over two positions. For **8-2Et$_2$O**, one of the *i*Pr groups was disordered over two positions. One of the solvent molecules on K^+ was disordered as a mixture of Et_2O and THF in a 74:26 ratio, refined by FVAR constants. The thermal ellipsoids were fixed by SHELXL restraints. For **10**, the co-crystallized THF molecule was disordered over two positions. The thermal ellipsoids were fixed by SHELXL restraints. These results were checked using the IUCR's CheckCIF routine. For **4** and **10**, the absolute structures could not be determined in chiral space groups and the alerts in the output are related to their Flack parameters. The other alerts in the output are related to the disordered groups and crystal solvents. CCDC 1898832–1898838 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

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Conflict of interest

The authors declare no conflict of interest.

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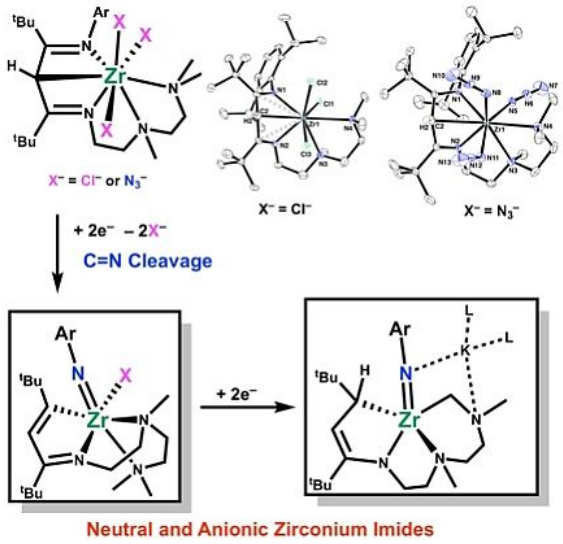

Neutral and Anionic Zirconium Imides

Takashi Kurogi, Jiaxiang Chu, Yaofeng Chen, Daniel J. Mindiola**

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Neutral and Anionic Monomeric Zirconium Imides Prepared via Selective C=N Bond Cleavage of a Multidentate and Sterically Demanding β-Diketiminato Ligand

A sterically encumbering multidentate β-diketiminato ligand, ^{tBu}L2, is reported in this study along with its coordination chemistry to zirconium(IV). Using the lithio salt of this ligand, Li(^{tBu}L2), the zirconium(IV) chloride and azide could be prepared and structurally characterized. Reduction of the ^{tBu}L2 zirconium(IV) complexes by KC_8 resulted in formation of mononuclear neutral and anionic zirconium imides via reductive cleavage of the imino group in the ^{tBu}L2 ligand.