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Synthesis and reactivity of neodymium(III) amido-tethered *N*-heterocyclic carbene complexes

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Abstract

The reaction of the heteroleptic Nd(III) iodide, [Nd(L')(N'')(μ-I)] with the potassium salts of primary aryl amides [KN(H)Ar'] or [KN(H)Ar*] affords heteroleptic, structurally characterised, low-coordinate neodymium amides [Nd(L')(N'')(N(H)Ar')] and [Nd(L')(N'')(N(H)Ar*)] cleanly (L' = *t*-BuNCH₂CH₂[C{NC(SiMe₃)CHN*t*-Bu}], N'' = N(SiMe₃)₂, Ar' = 2,6-Dipp₂C₆H₃, Dipp = 2,6-Pr^{*i*}₂C₆H₃, Ar* = 2,6-(2,4,6-Pr^{*i*}₃C₆H₂)₂C₆H₃). The potassium terphenyl primary amide [KN(H)Ar*] is readily prepared and isolated, and structurally characterised. Treatment of these primary amide-containing compounds with alkali metal alkyl salts results in ligand exchange to give alkali metal primary amides and intractable heteroleptic Nd(III) alkyl compounds of the form [Nd(L')(N'')(R)] (R = CH₂SiMe₃, Me). Attempted deprotonation of the Nd-bound primary amide in [Nd(L')(N'')(N(H)Ar*)] with the less nucleophilic phosphazene superbases Bu'N=P{N=P(NMe₂)₃}₃ resulted in indiscriminate deprotonations of peripheral ligand CH groups. **To cite this article:** P.L. Arnold, S.T. Liddle, C. R. Chimie 11 (2008).

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Résumé

La synthèse de complexes hétéroleptiques de néodyme à ligands amido-carbène [Nd(L')(N'')(N(H)Ar')] et [Nd(L')(N'')(N(H)Ar*)], réalisée par réaction de [KN(H)Ar'] ou de [KN(H)Ar*] avec les amidures de potassium [KN(H)Ar'] ou [KN(H)Ar*], est décrite (L' = *t*-BuNCH₂CH₂[C{NC(SiMe₃)CHN*t*-Bu}], N'' = N(SiMe₃)₂, Ar' = 2,6-Dipp₂C₆H₃, Dipp = 2,6-Pr^{*i*}₂C₆H₃, Ar* = 2,6-(2,4,6-Pr^{*i*}₃C₆H₂)₂C₆H₃). La synthèse et la structure d'un nouvel amidure de potassium [KN(H)Ar*] sont présentées. Les études structurales ont démontré que les complexes sont hétéroleptiques de coordination quatre. Des études de substitution ou de déprotonation sont présentées. Des expériences ont montré que les complexes hétéroleptiques de néodyme sont détruits lorsqu'ils sont mis en présence d'alkyls lithium ou potassium ; les complexes [Nd(L')(N'')(R)] (R = CH₂SiMe₃, Me) sont alors isolés. La déprotonation du complexe d'arylamide avec le « superbases »

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Bu'N=P{N=P(NMe₂)₃}₃ a démontré le caractère non régiospécifique de la déprotonation du ligand. *Pour citer cet article* : P.L. Arnold, S.T. Liddle, C. R. Chimie 11 (2008).

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Keywords: Neodymium; Lanthanide; *N*-Heterocyclic carbene; Amido; *N*-Ligand; Alkali metal; Phosphazene

Mots-clés : Néodyme ; Lanthanide ; Carbène hétérocyclique ; Amido ; *N*-ligand ; Métal alcalin ; Phosphazene

1. Introduction

The organometallic and coordination chemistry of low-coordinate lanthanide(III) complexes has greatly expanded in recent years and has generated a range of unusual f-block complexes. For example, complexes containing bonds between the lanthanide and main group metals including gallium, [Nd(L'){Ga(NArCH)₂}(N'')(THF)] (N'' = N(SiMe₃)₂, Ar = Dipp = 2,6-(Prⁱ₂C₆H₃) [1] and aluminium [Ln(Cp*)₂-Al(Cp*)] (Cp* = C₅Me₅) [2] have been isolated; the complexes [(N₂)(LnZ₂)₂] are formed from the reductive activation of dinitrogen by LnN''₃; molecular complexes of Nd(II), Tm(II), and Dy(II) have been isolated for the first time [3]; and a variety of reactions to activate inert substrates such as hydrocarbyl C–H and carbon dioxide C=O bonds have been reported [4].

Over the last decade, the organometallic chemistry of lanthanide complexes has been expanded to include a variety of *N*-heterocyclic carbene complexes, in which the carbene functions as a σ -donor to the electro-positive metal [5]. While the donor carbene complexes generally were not amenable to reductive activation chemistry [6], the σ -donor ligands did allow access to heteroleptic iodide complexes that were relatively inert to ligand scrambling [7]. This has allowed us to explore some metathetical routes to other low-coordinate lanthanide complexes.

The use of sterically encumbered ligands to make low-coordinate complexes is also of relevance to the continued search for isolable examples of terminal alkylidene and imido complexes of lanthanides [8].

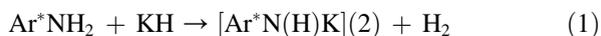
One major class of bulky group that can protect a reaction site at a metal comprises substituted terphenyls based on aryls, such as the Dipp- and Trip-functionalised systems Ar' = 2,6-Dipp₂C₆H₃ and Ar* = 2,6-Trip₂C₆H₃ (Dipp = 2,6-Prⁱ₂C₆H₃, Trip = 2,4,6-Prⁱ₃C₆H₂) [9].

Herein, we report the reactivity of the heteroleptic Nd(III) iodide [Nd(L)(I)(N'')] recently reported by us [5a], with primary arylamides, including the new potassium arylamide salt [KNHAr*], and the reactivity of these amido complexes towards nucleophiles and bases.

2. Results and discussion

2.1. Preparation of 2

Reaction of the terphenyl-substituted primary amine Ar*NH₂ [Ar* = 2,6-(2,4,6-Prⁱ₃C₆H₂)₂C₆H₃] with potassium hydride proceeds smoothly in THF to afford the corresponding potassium primary amide [KNHAr*] **2**, Eq. (1).



Following filtration and removal of solvent, compound **2** is isolated from hexane as an air- and moisture-sensitive yellow powder in good yield. The ¹H and ¹³C{¹H} NMR spectra are as expected; the most salient features are the broad singlet at 2.25 ppm in the ¹H NMR spectrum (*cf.* 2.06 ppm for the corresponding lithium salt reported by Power [10]), characteristic of an N–H group and the absence of any solvent resonances. The formulation of **2** as solvent free is corroborated by elemental analysis. We were unable to grow solvent free crystals of **2**, but yellow crystals of [2(OEt₂)₂] were readily obtained from a cold, saturated solution of **2** in diethyl ether. The diethyl ether in [2(OEt₂)₂] is bound very loosely as evidenced by rapid degradation, on exposure to dynamic vacuum, of crystals of [2(OEt₂)₂] to a yellow powder which affords NMR spectra identical to that of **2**, i.e. solvent free.

2.2. X-ray crystal structure of [2(OEt₂)₂]

The molecular structure of [2(OEt₂)₂] is illustrated in Fig. 1 and selected bond lengths and angles are presented in Table 1. Compound [2(OEt₂)₂] crystallises as a monomer; the potassium centre is pseudo tetrahedral, bonded to the anionic nitrogen, the neutral oxygen donors of two diethyl ether solvent molecules, and by an η^6 interaction to one of the Trip arene rings of the terphenyl group. The K(1)–N(1) bond length of 2.611(3) Å represents a rare example of a terminal primary amide–potassium bond and is short in comparison to other K–N bonds [from a survey of the Cambridge Structural Database version

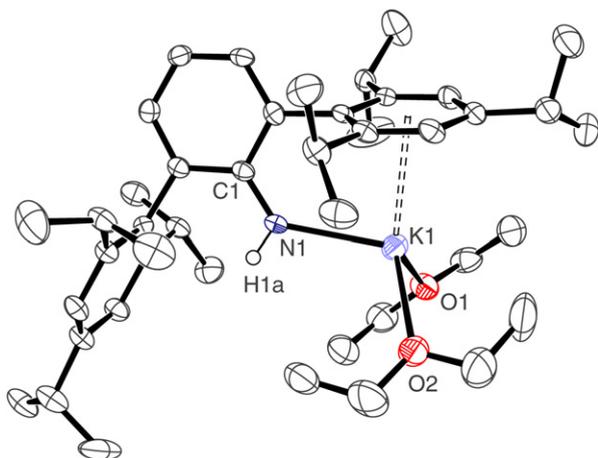


Fig. 1. Molecular structure of $[2(\text{OEt}_2)_2]$; carbon-bound hydrogen atoms omitted for clarity.

1.9], which are usually bridging, reflecting the formally low coordination number of potassium and the weak bonding nature of the donor groups. The $\text{K}\cdots\text{C}_{\text{aryl}}$ distances span the range 3.098(3)–3.463(3) Å, which is towards the lower end of the range of $\text{K}\cdots\text{C}_{\text{aryl}}$ distances [11].

2.3. Synthesis of **3** and **4**

Treatment of **1** with 1 equiv of $[\text{Ar}'\text{N}(\text{H})\text{K}]$ [12] in cold THF affords compound **3** as blue crystals, which, after workup and recrystallisation from *tert*-butyl methyl ether, are isolated in low yield, due to the high solubility of **3**, Scheme 1. The chemical shifts in the ^1H NMR spectrum fall in the range +65 to –15 ppm due to the paramagnetic neodymium(III) centre, but all resonances are observed. Similarly, treatment of **1** with 1 equiv of **2** in cold THF affords compound **4** as blue crystals in high yield after workup and recrystallisation from diethyl ether, Scheme 1. Both **3** and **4** are highly air- and moisture-sensitive. Crystals of **4** were shown to be the etherate $\mathbf{4}\cdot\frac{1}{3}\text{OEt}_2$ by X-ray crystallography (see below); exposure of crystals of **4** to dynamic vacuum results in loss of lattice solvent and collapse of the crystals into a blue glass. The ^1H NMR spectrum of **4** is resolved at room temperature over the range +54 → –20 ppm and is broader than that observed for **3**, perhaps reflecting the sterically more demanding environment around the neodymium(III) centre in **4** compared to **3**. Interestingly, solutions of **3** and **4** are dichroic; dilute solutions (or samples viewed through a short path length) appear pale blue whilst more concentrated (or longer path length) solutions appear dark red.

2.4. X-ray crystal structure of **3**

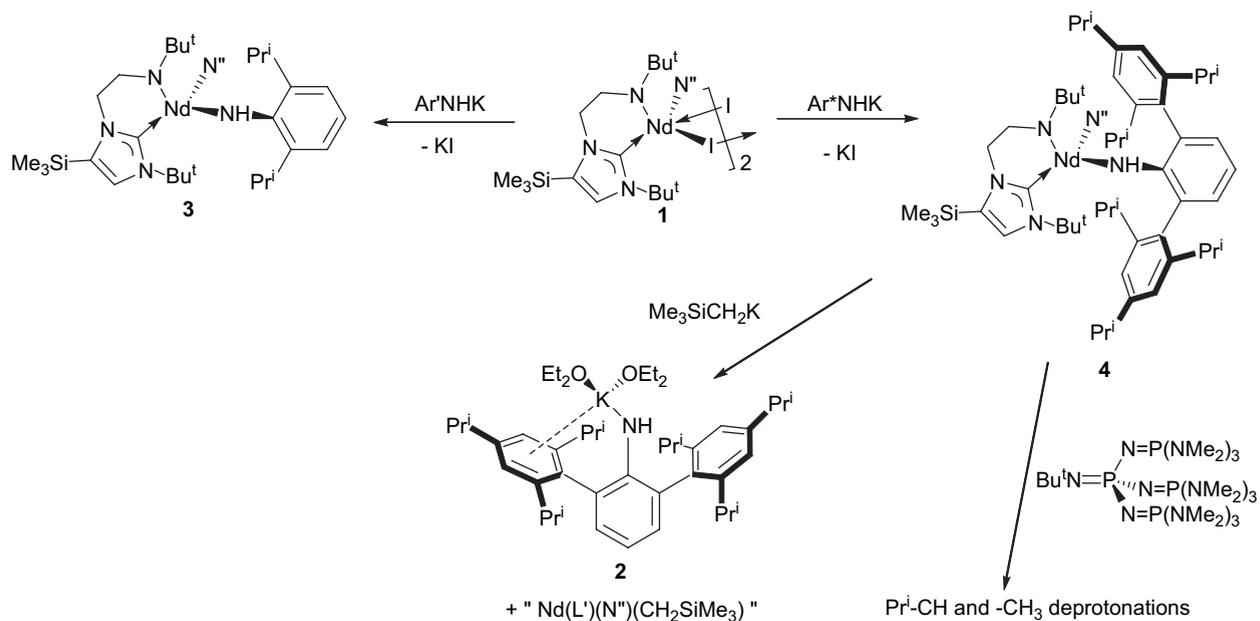
The molecular structure of **3** is depicted in Fig. 2 and selected bond lengths and angles are in Table 1. The four-coordinate neodymium centre adopts a distorted tetrahedral geometry, bonding to the neutral carbene centre of the NHC and the anionic nitrogen centres of the Dipp amide, N'' ligand, and amido tether of the NHC. The $\text{Nd}(1)\text{—C}(2)$ bond length of 2.612(4) Å is towards the lower end of Nd—C_{NHC} bonds which we have previously reported [7a] and statistically invariant compared to the Nd—C_{NHC} bond length of 2.609(3) Å in $[\text{Nd}(\text{L})(\text{N}'')_2]$, which also features a four-coordinate, distorted tetrahedral neodymium(III) centre [7a]. The $\text{Nd}(1)\text{—N}(2)$, $\text{Nd}(1)\text{—N}(5)$, and $\text{Nd}(1)\text{—N}(4)$ bond lengths of 2.252(3), 2.342(3), and 2.363(3) Å, respectively, are unexceptional, and follow the anticipated trend of $N_{\text{dialkyl}} < N_{\text{anilide}} < N_{\text{silyl}}$. The $\text{Nd}(1)\cdots\text{Si}(3)$ distance of 3.475 Å is suggestive of a close β -Si–C contact, and is corroborated by a smaller metal–amide–silicon angle at the amido nitrogen to $\text{Si}(3)$ of 116.38(16)° than that to $\text{Si}(2)$ which is 119.40(16)°. Similarly, the complex $[\text{Nd}(\text{L}')(\text{N}'')_2(\text{THF})]$ contains a close $\text{Nd—Si}(\text{N})$ distance of 3.353 Å to one silylamide group [7a], while the structure of $[\text{NdN}''_3]$ also contains an Nd—Si distance of 3.398 Å [13].

2.5. X-ray crystal structure of **4**

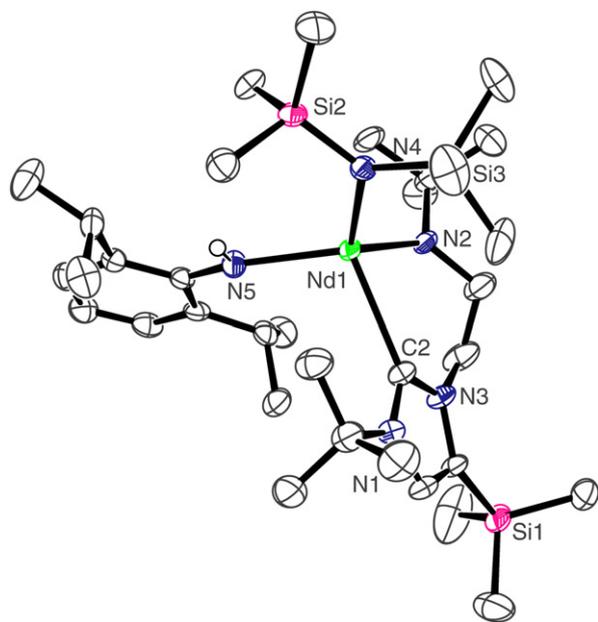
The molecular structure of compound **4** is shown in Fig. 3, and selected bond lengths and angles are in Table 1. Three molecules of **4** crystallise in the asymmetric unit but they differ from each other in only minor details so the structure of only one is discussed. As for **3**, the neodymium centre in **4** adopts a distorted tetrahedral geometry, bonding to the neutral carbene centre of the NHC and the anionic nitrogen centres of the terphenyl amide, N'' ligand, and amido tether of the NHC. The $\text{Nd}(1)\text{—C}(2)$ bond length of 2.603(6) Å is, statistically, essentially the same as in **3**. However, the Nd—C bond is much more distorted in **4** than it is in **3** as a consequence of the much greater steric demands of the terphenyl group compared to the Dipp group. We have previously described pitch and yaw, Fig. 4 [14], to quantify such deviations and the magnitude of the bends away from the ideal trigonal planar M—CN_2 moiety for **3** and **4** are 6.5° and 4.3° and 18.0° and 0.9°, respectively. Whereas the $\text{Nd}(1)\text{—N}(4)$ and $\text{Nd}(1)\text{—N}(5)$ bond lengths of 2.365(5) and 2.332(5) Å, respectively, in **4** are statistically invariant to the equivalent bonds in **3**, the $\text{Nd}(1)\text{—N}(2)$ bond length of 2.289(5) Å is slightly longer than the equivalent bond length in **3**, reflecting

Table 1
Selected bond lengths (Å) and angles (°) for **2**(OEt₂)₂, **3**, and **4**·1¹/₃ OEt₂

<i>2</i> (OEt ₂) ₂			
K(1)–N(1)	2.611(3)	K(1)–O(1)	2.719(3)
K(1)–O(2)	2.715(3)	K(1)–C(7)	3.115(3)
K(1)–C(8)	3.098(3)	K(1)–C(9)	3.269(3)
K(1)–C(10)	3.463(3)	K(1)–C(11)	3.442(3)
K(1)–C(12)	3.296(3)		
N(1)–K(1)–O(2)	106.13(9)	N(1)–K(1)–O(1)	109.15(9)
O(2)–K(1)–O(1)	103.70(8)	N(1)–K(1)–C(8)	69.50(9)
O(2)–K(1)–C(8)	105.85(9)	O(1)–K(1)–C(8)	149.48(9)
N(1)–K(1)–C(7)	58.22(8)	O(2)–K(1)–C(7)	130.32(9)
O(1)–K(1)–C(7)	125.89(8)	C(8)–K(1)–C(7)	26.26(8)
N(1)–K(1)–C(9)	94.33(9)	O(2)–K(1)–C(9)	99.04(9)
O(1)–K(1)–C(9)	140.79(9)	C(8)–K(1)–C(9)	24.83(8)
C(7)–K(1)–C(9)	44.36(9)	N(1)–K(1)–C(12)	75.94(8)
O(2)–K(1)–C(12)	148.60(9)	O(1)–K(1)–C(12)	105.02(8)
C(8)–K(1)–C(12)	44.48(8)	C(7)–K(1)–C(12)	25.27(8)
C(9)–K(1)–C(12)	49.92(8)	N(1)–K(1)–C(11)	99.15(8)
O(2)–K(1)–C(11)	134.76(9)	O(1)–K(1)–C(11)	102.47(8)
C(8)–K(1)–C(11)	49.91(9)	C(7)–K(1)–C(11)	43.15(8)
C(9)–K(1)–C(11)	41.36(8)	C(12)–K(1)–C(11)	23.82(8)
N(1)–K(1)–C(10)	108.37(8)	O(2)–K(1)–C(10)	111.76(9)
O(1)–K(1)–C(10)	117.14(9)	C(8)–K(1)–C(10)	43.07(9)
C(7)–K(1)–C(10)	50.68(8)	C(9)–K(1)–C(10)	23.66(8)
C(12)–K(1)–C(10)	42.16(8)	C(11)–K(1)–C(10)	23.17(8)
<i>Compound 3</i>			
Nd(1)–N(2)	2.252(3)	Nd(1)–N(5)	2.342(3)
Nd(1)–N(4)	2.363(3)	Nd(1)–C(2)	2.612(4)
N(1)–C(2)	1.360(5)	N(3)–C(2)	1.372(5)
N(2)–Nd(1)–N(5)	121.92(12)	N(2)–Nd(1)–N(4)	11.14(12)
N(5)–Nd(1)–N(4)	108.84(11)	N(2)–Nd(1)–C(2)	79.17(12)
N(5)–Nd(1)–C(2)	105.69(12)	N(4)–Nd(1)–C(2)	122.76(12)
Nd(1)–N(4)–Si(2)	119.40(16)	N(1)–C(2)–N(3)	102.9(3)
Nd(1)–N(4)–Si(3)	116.38(16)		
<i>4</i> ·1 ¹ / ₃ OEt ₂			
Nd(1)–N(2)	2.289(5)	Nd(1)–N(5)	2.332(5)
Nd(1)–N(4)	2.365(5)	Nd(1)–C(2)	2.603(6)
N(1)–C(2)	1.355(7)	N(3)–C(2)	1.362(7)
Nd(1A)–N(2A)	2.270(5)	Nd(1A)–N(5A)	2.326(5)
Nd(1A)–N(4A)	2.366(5)	Nd(1A)–C(2A)	2.602(6)
N(1A)–C(2A)	1.366(7)	N(3A)–C(2A)	1.362(7)
Nd(1B)–N(2B)	2.269(5)	Nd(1B)–N(5B)	2.338(4)
Nd(1B)–N(4B)	2.361(5)	Nd(1B)–C(2B)	2.603(7)
N(1B)–C(2B)	1.357(7)	N(3B)–C(2B)	1.364(7)
N(2)–Nd(1)–N(5)	97.97(17)	N(2)–Nd(1)–N(4)	110.55(17)
N(5)–Nd(1)–N(4)	133.43(17)	N(2)–Nd(1)–C(2)	84.07(17)
N(5)–Nd(1)–C(2)	110.61(17)	N(4)–Nd(1)–C(2)	108.36(18)
N(1)–C(2)–N(3)	103.0(5)	N(2A)–Nd(1A)–N(5A)	100.55(18)
N(2A)–Nd(1A)–N(4A)	111.3(2)	N(5A)–Nd(1A)–N(4A)	129.60(18)
N(2A)–Nd(1A)–C(2A)	81.64(19)	N(5A)–Nd(1A)–C(2A)	104.55(19)
N(4A)–Nd(1A)–C(2A)	117.60(19)	N(3A)–C(2A)–Nd(1A)	120.3(4)
N(2B)–Nd(1B)–N(5B)	95.57(16)	N(2B)–Nd(1B)–N(4B)	112.06(17)
N(5B)–Nd(1B)–N(4B)	133.17(17)	N(2B)–Nd(1B)–C(2B)	84.37(18)
N(5B)–Nd(1B)–C(2B)	106.59(17)	N(4B)–Nd(1B)–C(2B)	112.89(18)
N(1B)–C(2B)–N(3B)	103.2(5)		

Scheme 1. Synthesis of **2** and **4**, and reactions of **4**.

the greater steric congestion at neodymium in **4** compared to **3**. As in **3**, an Nd(1)⋯Si(3) distance of 3.419 Å in **4** is suggestive of a β-Si–C contact due to the low coordination number of neodymium.

Fig. 2. Molecular structure of **3**; carbon-bound hydrogen atoms omitted for clarity.

2.6. Reactivity of **3** and **4** towards alkali metal alkyls

In an effort to deprotonate the primary amide in **3** and **4** a second time to afford anionic imido species, **3** and **4** were treated with alkali metal alkyls MR (M = Li or K, R = Me or CH₂SiMe₃). In the case of **3**, intractable, oily products were obtained which we were unable to unambiguously identify due to the paramagnetic nature of neodymium(III). However, treatment of **4** with alkali metal alkyls led to isolable products; in each case, the corresponding alkali metal terphenyl amide [Ar*N(H)M] (M = Li or K) was eliminated affording heteroleptic species of the general form [Nd(L')(N'')(R)], which doubtless undergo Schlenk-type equilibria. The identities of [Ar*N(H)Li] [15] and **2** were confirmed by comparison of their NMR spectra with authentic samples, and by a unit cell determination of the latter crystallised as 2(OEt₂)₂ (see above).

2.7. Reactivity of **4** towards the phosphazene superbase Bu^tN=P{N=P(NMe₂)₃}₃

Since the primary aryl amide ligands had proven to be vulnerable to ligand exchange in the presence of strong nucleophiles such as alkyls, apparently a process thermodynamically more favourable compared to double deprotonation of the primary amide centre, the

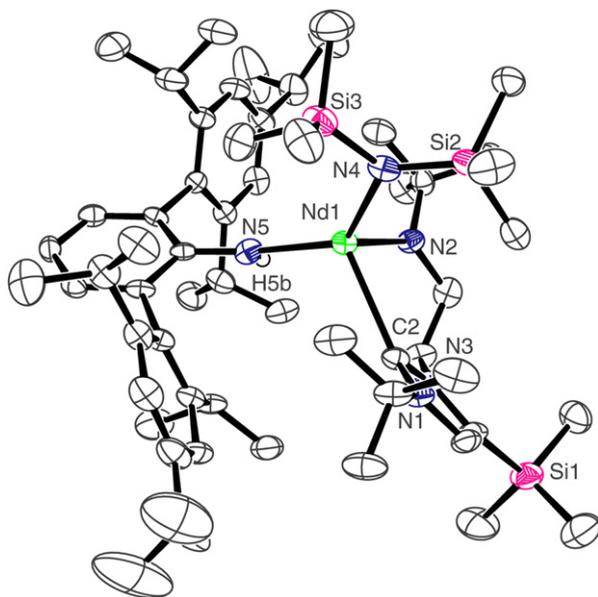


Fig. 3. Molecular structure of **4**; carbon-bound hydrogen atoms omitted for clarity.

reaction of **4** with the bulky phosphazene superbases $\text{Bu}'\text{N}=\text{P}\{\text{N}=\text{P}(\text{NMe}_2)_3\}_3$ was attempted, Scheme 1, since it is a base with great thermodynamic strength but very poor nucleophilicity [16]. Treatment of **4** with 1 equiv of $\text{Bu}'\text{N}=\text{P}\{\text{N}=\text{P}(\text{NMe}_2)_3\}_3$ afforded an intractable brown oil which could not be recrystallised despite exhaustive attempts. In order to gain insight as to the nature of the reaction product(s) an aliquot was quenched with D_2O and a ^2H NMR spectrum obtained. The resulting spectrum exhibited broad ^2H resonances at 1.82, 3.14, 4.16, and 6.91 ppm, characteristic of *ortho*- and *para*-methyl and methine deprotonations of the *iso*-propyl groups as well as minor deprotonation at the aryl *para* position of the terphenyl ligand. Due to the bulk of the phosphazene superbases and the steric congestion around the amide–proton linkage we suggest that deprotonation at the C–H sites must be kinetically more favourable than removal of the amide proton, despite the latter being surely more acidic than the former grouping (for analogous reactivity of a phosphazene superbases

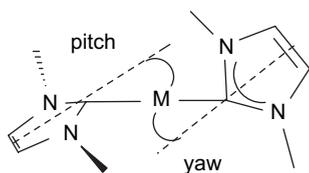


Fig. 4. Illustration of pitch and yaw in metal–NHC complexes.

with a scandium amide supported by a β -diketiminato ligand system see Ref. [17]).

3. Conclusions

The potassium terphenyl primary amide $[\text{Ar}'\text{N}(\text{H})\text{K}]$ (**2**) is readily prepared and isolated in high yield. The reaction of $[\text{Nd}(\text{L}')(\text{N}'')(\mu\text{-I})]$ (**1**) with 1 equiv of $[\text{Ar}'\text{N}(\text{H})\text{K}]$ or **2** affords **3** and **4** cleanly. Both complexes exhibit four-coordinate, tetrahedral Nd(III) centres supplemented by β -Si–C interactions. Treatment of **3** or **4** with alkali metal alkyls results in ligand exchange to give alkali metal primary amides and heteroleptic species of the generic form $[\text{Nd}(\text{L}')(\text{N}'')(\text{R})]$, which are intractable. Treatment of **4** with the thermodynamically more basic, but less nucleophilic phosphazene superbases $\text{Bu}'\text{N}=\text{P}\{\text{N}=\text{P}(\text{NMe}_2)_3\}_3$ results in indiscriminate deprotonations at *iso*-propyl methyl and methine sites and the terphenyl aryl *para* position, which we ascribe to the greater kinetic accessibility of these sites compared to the amide–proton linkage.

4. Experimental

4.1. General

All manipulations were carried out using standard Schlenk techniques, or an MBraun UniLab glovebox, under an atmosphere of dry nitrogen. Hexane, diethyl ether and THF were dried by passage through activated alumina towers and degassed before use. Benzene and *tert*-butyl methyl ether were distilled from potassium under an atmosphere of dry nitrogen. All solvents were stored over potassium mirrors (with the exception of THF which was stored over activated 4 Å molecular sieves). Deuterated benzene was distilled from potassium, degassed by three freeze–pump–thaw cycles and stored under nitrogen. The compounds $[\text{MeK}]$ [18], $[\text{Me}_3\text{SiCH}_2\text{K}]$ [11b], $[\text{Ar}'\text{N}(\text{H})\text{K}]$ [12], $\text{Ar}'\text{NH}_2$ [14], and **1** [7a] were prepared by published literature procedures [$\text{Ar}' = 2,6\text{-Pr}_2\text{C}_6\text{H}_3$; $\text{Ar}'' = 2,6\text{-}(2,4,6\text{-Pr}_3\text{C}_6\text{H}_2)_2\text{C}_6\text{H}_3$]. $\text{Bu}'\text{N}=\text{P}\{\text{N}=\text{P}(\text{NMe}_2)_3\}_3$ (1.0 M in hexane), $[\text{MeLi}]$ (1.6 M in diethyl ether) and $[\text{Me}_3\text{SiCH}_2\text{Li}]$ (1.0 M in pentane) were purchased from Aldrich and used as supplied.

^1H , ^{13}C , and ^{31}P NMR spectra were recorded on a Bruker 300 spectrometer operating at 300.1, 75.5, and 121.5 MHz, respectively; chemical shifts are quoted in ppm and are relative to TMS (^1H and ^{13}C) and external 85% H_3PO_4 (^{31}P). Elemental microanalyses were carried out by Mr. Stephen Boyer at

the Microanalysis Service, London Metropolitan University, UK.

4.2. Preparation of $[Ar^*N(H)K]$ (**2**)

THF (60 ml) was added to a mixture of Ar^*NH_2 (6.92 g, 13.90 mmol) and KH (1.50 g, 37.00 mmol) and the resulting suspension was refluxed for 5 days. The mixture was filtered to give a green-brown solution and volatiles were removed *in vacuo* to give a sticky yellow solid. The solid was washed with hexane (50 ml) and dried *in vacuo* to afford **2** as a free flowing yellow powder. The hexane washing was concentrated until precipitation occurred and then stored at $-30^\circ C$ overnight. The resultant yellow powder was collected by filtration and dried. Combined yield: 5.77 g, 78%. Yellow crystals of $[2(OEt_2)_2]$ were obtained from a saturated solution in diethyl ether stored at $-30^\circ C$ overnight; the diethyl ether is weakly bound, as evidenced by the collapse of single crystals to a yellow powder on exposure to vacuum and the CHN microanalysis. Anal. Calcd for $C_{36}H_{50}KN$: C, 80.69; H, 9.40; N, 2.61. Found: C, 80.58; H, 9.56; N, 2.63. 1H NMR (benzene- d_6 , 295 K): δ 1.28 (d, $^3J_{HH} = 6.91$ Hz, 12H, *para*-CH(CH_3) $_2$), 1.35 (d, $^3J_{HH} = 6.86$ Hz, 24H, *ortho*-CH(CH_3) $_2$), 2.25 (s, br, 1H, NH), 2.94 (sept, $^3J_{HH} = 6.91$ Hz, 2H, *para*-CH(CH_3) $_2$), 3.41 (sept, $^3J_{HH} = 6.86$ Hz, 4H, *ortho*-CH(CH_3) $_2$), 6.62 (t, $^3J_{HH} = 7.20$ Hz, 1H, *para*-Ar-CH), 7.08 (d, $^3J_{HH} = 7.20$ Hz, 2H, *meta*-Ar-CH) and 7.22 (s, 4H, *meta*-Tripp-CH). $^{13}C\{^1H\}$ NMR (benzene- d_6 , 295 K): δ 24.29 (*ortho*-CH(CH_3) $_2$), 24.93 (*para*-CH(CH_3) $_2$), 30.36 (*ortho*-CH(CH_3) $_2$), 34.34 (*para*-CH(CH_3) $_2$), 107.10 (*para*-Ar-CH), 120.43 (*meta*-Tripp-CH), 123.71 (*meta*-Ar-CH), 129.59 (*para*-Tripp-C), 141.15 (*ortho*-Ar-C), 146.98 (*ortho*-Tripp-C), 148.72 (*ipso*-Tripp-C) and 161.59 (*ipso*-Ar-C).

4.3. Preparation of $[Nd(L')(N'')(NHA r^*)]$ (**3**)

A solution of $[Ar^*N(H)K]$ (0.43 g, 2.01 mmol) in THF (10 ml) was added dropwise to a solution of **1** (1.46 g, 2.01 mmol) in THF (5 ml). The mixture was stirred overnight prior to volatiles being removed *in vacuo*. The mixture was extracted with diethyl ether (30 ml), filtered, and volatiles removed *in vacuo* to give a 'foamy' pale blue oil. The oil was dissolved in *tert*-butyl methyl ether (1.5 ml) and stored at $-30^\circ C$ for 5 days to afford a crop of blue crystals of **3**. Yield: 0.60 g, 38%. Anal. Calcd for $C_{34}H_{68}N_5NdSi_3$: C, 52.66; H, 8.84; N, 9.03. Found: C, 52.47; H, 8.78; N, 9.00. 1H NMR (benzene- d_6 , 295 K): δ -14.45 (s, 9H, C(CH_3) $_3$), -7.71 (s, 9H, C(CH_3) $_3$), -2.28 (s, 18H, Si(CH_3) $_3$), -0.03 (s, 9H, Si(CH_3) $_3$), 0.43

(s, 1H, CH(CH_3) $_2$), 1.00 (s, 1H, CH(CH_3) $_2$), 3.21 (s, 6H, CH(CH_3) $_2$), 4.59 (s, 6H, CH(CH_3) $_2$), 7.97 (t, $^3J_{HH} = 7.29$ Hz, *para*-Ar'-CH), 12.20 (d, $^3J_{HH} = 7.29$ Hz, 2H, *meta*-Ar'-CH), 19.00 (s, 1H, CH_2), 24.03 (s, 1H, CH_2), 24.48 (s, 1H, C=CH), 46.83 (s, br, 1H, NH), 63.95 (s, 1H, CH_2) and 65.09 (s, 1H, CH_2).

4.4. Preparation of $[Nd(L')(N'')(NHA r^*)]$ (**4**)

THF (80 ml) was added to a cold ($-78^\circ C$) mixture of **1** (5.48 g, 7.55 mmol) and **2** (4.05 g, 7.55 mmol) and the resulting mixture was allowed to warm slowly to room temperature with stirring overnight. The solution was filtered, and volatiles removed *in vacuo* from the orange-brown solution to give a 'foamy' pale blue oil. The oil was dissolved in diethyl ether (6 ml) and stored at $5^\circ C$ overnight to afford blue crystals of $4 \cdot 1\frac{1}{3} OEt_2$; the diethyl ether is weakly held in the crystal lattice as evidenced by the collapse of crystals of **4** to a 'foamy' blue oil on prolonged exposure to vacuum and the CHN microanalysis. Yield: 7.48 g, 83%. Anal. Calcd for $C_{58}H_{100}N_5NdSi_3$: C, 63.56; H, 9.20; N, 6.39. Found: C, 63.48; H, 9.27; N, 6.22. 1H NMR (benzene- d_6 , 295 K): δ -19.81 (s, br, 9H, C(CH_3) $_3$), -7.71 (s, br, 9H, C(CH_3) $_3$), -1.14 (s, 18H, Si(CH_3) $_3$), 0.22 (s, 4H, *ortho*-CH(CH_3) $_2$), 0.97 (s, br, 12H, *para*-CH(CH_3) $_2$), 0.99 (s, 9H, Si(CH_3) $_3$), 2.35 (s, 2H, *para*-CH(CH_3) $_2$), 3.40 (s, br, 24H, *ortho*-CH(CH_3) $_2$), 7.12 (s, 4H, *meta*-Tripp-CH), 8.87 (s, 1H, *para*-Ar-CH), 11.89 (s, 2H, *meta*-Ar-CH), 16.56 (s, br, 2H, CH_2), 25.63 (s, br, 1H, C=CH), 47.10 (s, br, 1H, NH) and 53.57 (s, br, 2H, CH_2).

4.5. General procedure for reaction of **3** or **4** with group 1 alkyls

A solution of diethyl ether (20 ml) was added to a cold ($-78^\circ C$) mixture of **3** or **4** (1.00 mmol) and solid $[Me_3SiCH_2M]$ or $[MeM]$ ($M = Li$ or K) (1.00 mmol). The mixture was allowed to slowly warm to room temperature with stirring overnight. Only $[Ar^*N(H)M]$ ($M = Li$ or K) could be isolated from reaction mixtures, as confirmed by comparison of their NMR spectra with authentic samples and by a unit cell determination of the latter crystallised as $2(OEt_2)_2$.

4.6. Reaction of **4** with $Bu^iN=P\{N=P(NMe_2)_3\}_3$

A solution of $Bu^iN=P\{N=P(NMe_2)_3\}_3$ (1.32 g, 2.08 mmol) in benzene (10 ml) was added dropwise to a solution of **4** (2.27 g, 2.08 mmol) in benzene (10 ml)

Table 2

Crystal data for 2(OEt)₂, **3**, and 4·1¹/₃ OEt₂

	2(OEt) ₂	3	4·1 ¹ / ₃ OEt ₂
Formula	C ₄₄ H ₇₀ KNO ₂	C ₃₄ H ₆₈ N ₅ NdSi ₃	C _{63.33} H _{113.33} N ₅ NdO _{1.33} Si ₃
Formula weight	684.11	775.44	1194.77
Crystal size, mm	0.22 × 0.27 × 0.32	0.31 × 0.33 × 0.38	0.37 × 0.44 × 0.48
Crystal system	Triclinic	Triclinic	Triclinic
Space group	<i>P</i> –	<i>P</i> –	<i>P</i> –
<i>a</i> , Å	9.741(2)	12.4161(8)	16.7142(9)
<i>b</i> , Å	12.294(3)	12.7123(8)	26.6355(14)
<i>c</i> , Å	18.274(4)	15.7210(10)	27.1609(15)
α , °	99.954(3)	109.104(2)	65.480(2)
β , °	93.269(3)	99.689(2)	74.110(2)
γ , °	90.137(3)	108.166(2)	89.535(2)
<i>V</i> , Å ³	2151.7(8)	2124.4(2)	10,503.7(10)
<i>Z</i>	2	2	6
ρ_{calcd} , g cm ^{−3}	1.056	1.212	1.133
μ , mm ^{−1}	0.157	1.333	0.832
No. of reflections measured	14,669	14,864	97,847
No. of unique reflections, <i>R</i> _{int}	7528, 0.0572	7429, 0.0238	36,779, 0.0695
No. of reflections <i>F</i> ² > 2σ(<i>F</i> ²)	3862	6620	4207
Transmission coefficient range	0.703–0.970	0.631–0.683	0.891–0.919
<i>R</i> , <i>R</i> _w ^a (<i>F</i> ² > 2σ)	0.0585, 0.1309	0.0417, 0.1042	0.0659, 0.1377
<i>R</i> , <i>R</i> _w ^a (all data)	0.1412, 0.1655	0.0481, 0.1086	0.1234, 0.1544
<i>S</i> ^a	0.982	1.076	0.925
Parameters	449	410	1945
Max., min. difference map, e Å ^{−3}	0.304, −0.372	4.111, −1.202	2.463, −2.389

^a Conventional $R = \sum |F_o| - |F_c| / \sum |F_o|$; $R_w = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}$; $S = [\sum w(F_o^2 - F_c^2)^2 / (\text{No. data} - \text{No. parameters})]^{1/2}$ for all data.

to give a green-red solution. The mixture was stirred overnight, then volatiles were removed *in vacuo*. Crude ³¹P{¹H} NMR (benzene-*d*₆, 295 K): δ 5.90 (d, ²*J*_{PP} = 17.98 Hz) and −24.28 (q, ²*J*_{PP} = 17.98 Hz). Following exhaustive attempts at recrystallisation, a portion of the sample was hydrolysed with D₂O and a ²H NMR spectrum (benzene, 295 K) was recorded, which exhibited broad resonances at δ 1.82 (*ortho*-CH(CH₂D)(CH₃)), 3.14 (*para*-CH(CH₂D)(CH₃)), 4.16 (*ortho*- and *para*-CD(CH₃)₂) and 6.91 (*para*-Ar-CD).

4.7. X-ray crystallography

Crystal data for compounds 2(OEt)₂, **3**, and 4·1¹/₃ OEt₂ are given in Table 2. Crystals were examined on a Bruker AXS 1000 or Apex CCD area detector diffractometer using graphite-monochromated Mo K α radiation ($\lambda = 0.71073$ Å). Intensities were integrated from a sphere of data recorded on narrow (0.3°) frames by ω rotation. Cell parameters were refined from the observed positions of all strong reflections in each data set. Semi-empirical absorption corrections were applied, based on symmetry-equivalent and repeat reflections. The structures were solved by direct methods and were refined by least-squares methods on all unique *F*² values, with anisotropic displacement parameters, and

with constrained riding hydrogen geometries; *U*(H) was set at 1.2 (1.5 for methyl groups) times *U*_{eq} of the parent atom. The largest features in final difference syntheses were close to heavy atoms. A highly disordered diethyl ether solvent molecule of crystallisation in **3** could not be modelled and was treated with the Platon SQUEEZE procedure [19]. Programs were Bruker AXS SMART (control) and SAINT (integration) [20], and SHELXTL for structure solution, refinement, and molecular graphics [21]. The supplementary material has been sent to the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK (CCDC# 658923–658925) and can be obtained by contacting the CCDC (quoting the article details and the corresponding SUP number).

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