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NMR spectroscopic study of the adduct formation and reactivity of homoleptic rare earth amides with alkali metal benzyl compounds, and the crystal structures of $[\text{Li}(\text{TMEDA})_2][\text{Nd}\{\text{N}(\text{SiMe}_3)_2\}_3(\text{CH}_2\text{Ph})]$ and $\{\{\text{Li}(\text{TMP})\}_2\{\text{Li}(\text{Ph})\}\}_2$

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ABSTRACT

An NMR spectroscopic study has been conducted into the reactivity of alkali metal benzyls $[\text{M}(\text{CH}_2\text{Ph})]$, ($\text{M} = \text{Li}, \text{Na}, \text{K}$) with lanthanide tris(amide) complexes $[\text{Ln}(\text{N}'')_3]$ ($\text{Ln} = \text{Y}, \text{Ce}, \text{Nd}$; $\text{N}'' = \text{N}(\text{SiMe}_3)_2$) and $[\text{Ce}(\text{TMP})_3]$ ($\text{TMP} = 2,2,6,6\text{-tetramethylpiperidide}$). It was found that for $[\text{Ln}(\text{N}'')_3]$, benzyl adducts $[\text{M}][\text{Ln}(\text{N}'')_3(\text{CH}_2\text{Ph})]$ were initially formed, and the molecular structure for $\text{M} = \text{Li}(\text{TMEDA})_2$ and $\text{Ln} = \text{Nd}$ was determined revealing a distorted tetrahedral $[\text{Nd}(\text{N}'')_3(\text{CH}_2\text{Ph})]$ anion. In all cases, these adduct complexes were unstable, intramolecularly deprotonating a methyl arm of a N'' ligand via benzyl basicity and eliminating toluene to prepare cyclometallated complexes of the form $[\text{M}][\text{Ln}(\text{N}'')_2\{\kappa^2\text{-CH}_2\text{Si}(\text{Me})_2\text{N}(\text{SiMe}_3)\}]$. In parallel studies, reactions of $[\text{Li}(\text{Ph})]$ with $[\text{Ln}(\text{N}'')_3]$ ($\text{Ln} = \text{Ce}, \text{Nd}$) afforded $[\text{Li}(\text{N}'')]$, whilst for ($\text{Ln} = \text{Y}$) adduct formation was observed. $[\text{Ce}(\text{TMP})_3]$ did not generate any characterisable bimetallic adducts. The reaction of $[\text{Li}(\text{Ph})]$ with $[\text{Li}(\text{TMP})]$ afforded the hexanuclear $\{\{\text{Li}(\text{TMP})\}_2\{\text{Li}(\mu\text{-Ph})\}\}_2$, which features lithium in three different coordination environments.

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1. Introduction

Research into mixed-metal organometallics has demonstrated that certain bi- and multi-metallic compounds have patterns of reactivity that can be both wider in scope and more selective than the individual components on their own [1]. This has led to the systematic development of mixed-metal compounds with synergic reactivity [2] that have many potential applications including selective metalation reactions [3] for more efficient organic synthesis [4], as well as for use in catalysis (e.g. mixed f-block/Mg polymerisation catalysts) [5,6]. One particularly well known example of enhanced reactivity of a bimetallic system is the widely used Lochmann-Schlosser base, which is a mixture of *n*-butyllithium and potassium *tert*-butoxide [3].

Alkali metal secondary amides – in particular $[\text{M}\{\text{N}(\text{Pr})_2\}]$, $[\text{M}$

$\{\text{N}(\text{SiMe}_3)_2\}]$ and $[\text{M}(\text{TMP})]$; $\text{M} = \text{Li}, \text{Na}, \text{K}$; $\text{TMP} = 2,2,6,6\text{-tetramethylpiperidide}$ – are ubiquitous throughout synthetic chemistry [7], and their synergic behaviour with, for example, Mg, Mn and Zn organometallics leads to unusual reactivity that can be understood through detailed knowledge of the structure of these reagents (e.g. **1**, Fig. 1) [1,3]. Rare earth amides and organometallics, on the other hand, are not widely used throughout chemistry with their use mainly restricted to synthetic f-block chemistry [8]. Simple homoleptic starting materials, such as $[\text{Ln}(\text{N}'')_3]$ [9] and $[\text{Ln}\{\text{CH}(\text{SiMe}_3)_2\}_3]$ [10–12], and the THF solvated $[\text{Ln}(\text{CH}_2\text{Ph})_3(\text{THF})_n]$ ($n = 2$ [13,14] or 3 [13–16]) and $[\text{Ln}(\text{CH}_2\text{SiMe}_3)_3(\text{THF})_n]$ ($n = 2$ [17,18] or 3 [17,19]), are well known, although they are very air- and moisture-sensitive and can be non-trivial to synthesise. The rare earth elements, with their large ionic radii, high coordination numbers and interactions dominated by ionic bonding, also have a well-developed ‘ate’ chemistry producing charge separated lanthanide complexes when additional anionic ligands bind to the Ln metal centres [20]. Examples of charge-separated organometallic lanthanide ‘ate’ compounds include $[\text{Li}(\text{L})_n][\text{LnR}_4]$ ($\text{R} = \text{tBu}$ [21–23], CH_2SiMe_3 [22,24,25]; ($\text{L})_n = (\text{THF})_4, (\text{TMEDA})_2, (\text{DME})_3$; $\text{DME} = \text{MeOC}_2\text{H}_4\text{OMe}$), the heteroleptic $[\text{Li}(\text{DME})_3][\text{Nd}(\text{Cp})_3(\text{Ph})]$

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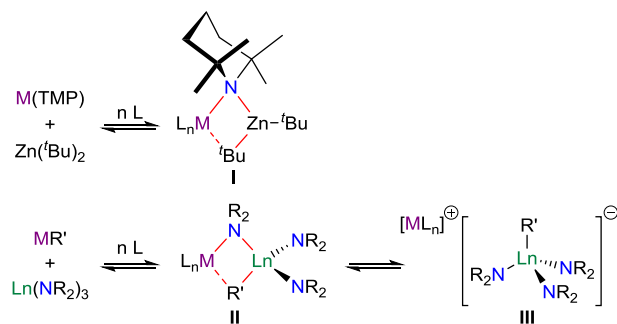


Fig. 1. Bimetallic mixed-metal organometallic compounds.

[26] and $[\text{Yb}^{\text{II}}(\text{CH}_2\text{Ph})(\text{THF})_5][\text{Yb}^{\text{III}}(\text{CH}_2\text{Ph})_4(\text{THF})_2]$ which formed in preference to neutral $[\text{Yb}^{\text{III}}(\text{CH}_2\text{Ph})_3(\text{THF})_3]$ [13]. Contacted ion-pairs are also known (Fig. 2, top), for example, with Me: $[\text{Ln}\{\mu\text{-Me}\}_2\text{Li}(\text{TMEDA})]_3$ [27,28], $\text{N}(\text{iPr})_2$: $[\text{Li}(\mu\text{-N}^i\text{Pr}_2)_2\text{Y}(\text{N}^i\text{Pr}_2)_2]$ [29], N'' : $[\text{Li}(\mu\text{-N}'')_2\text{Ln}^{\text{II}}\text{N}'']$ [30] and CH_2Ph : $[\text{K}(\text{THF})\text{K}(\text{THF})_2\text{Sc}(\mu\text{-CH}_2\text{Ph})_5]$, which contains a complicated extended structure in the solid state [15].

We were interested in lanthanide motifs with two different bridging atoms similar to I, because only a handful of structurally characterised examples are known (Fig. 2, bottom) that show lanthanide complexes with mixed alkyl/amide bridging interactions (type II, Fig. 1) [31–33]. These include cyclometallated complexes that result from N'' ligand deprotonation [34–36], such as $[\text{K}\{\text{Y}(\text{N}'')_2\{\kappa^2\text{-CH}_2\text{Si}(\text{Me})_2\text{N}(\text{SiMe}_3)\}}]$ [30] that becomes a solvent separated ion pair when a co-ligand such as 18-crown-6 is used [37]. These cyclometallated structures demonstrate one potential drawback from using the ubiquitous N'' anion as a supporting ligand because group 1 organometallics are strong bases; $[\text{Na}(\text{N}'')]$, $[\text{K}\{\text{Si}(\text{SiMe}_3)_3\}]$ and ${}^t\text{BuLi}/\text{TMEDA}$ react with $[\text{Ln}(\text{N}'')_3]$ ($\text{Ln} = \text{Y}, \text{Yb}$) to deprotonate the N'' ligand forming a dianionic ($\kappa^2\text{-N,C}$) ligand [30,34] instead of generating a stable bimetallic adduct. In contrast, the reaction of $[\text{Yb}(\text{N}'')_3]$ with ${}^t\text{BuLi}$ caused reduction to $\text{Yb}(\text{II})$ and formation of $[\text{LiYb}(\text{N}'')_3]$ [30].

Synergic reactivity based upon bimetallic complexes of group 1 and the rare earths has not been systematically investigated, so this paper details our first investigations in this field targeting bimetallic complex formation using weaker bases than butyl lithium (type II). We show that adducts are initially formed, which can be

stable for several days, long enough to crystallise a heteroleptic Nd ‘ate’ species (type III, Fig. 1).

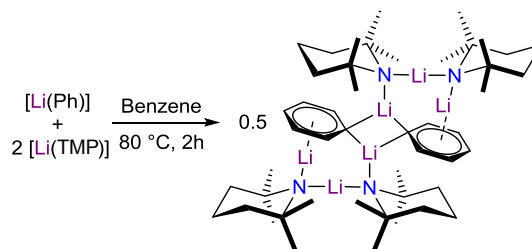
2. Results and discussion

2.1. Homometallic species

Initially, we investigated the reaction of a lithium organometallic with a lithium amide in order to study adduct formation using the same very electropositive metal (Pauling electronegativity, χ_{P} of Li = 0.98) [38]. This would allow us to investigate ligand compatibility and bonding modes that could then be applicable to heterobimetallic systems including rare earth elements.

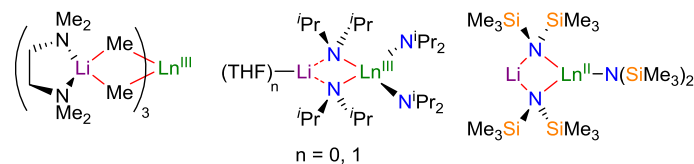
The 1:1 reaction of $[\text{Li}(\text{Ph})]$ with $[\text{Li}(\text{TMP})]$ in benzene at 80°C for 2 h afforded a brown suspension, wherein only some of the lithium phenyl was observed to dissolve. Upon cooling, pale yellow crystals suitable for X-ray diffraction studies were grown, which revealed this complex to be the hexanuclear species $[\{\text{Li}(\text{TMP})\}_2\{\text{Li}(\mu\text{-Ph})\}_2]$ (1). Repeating the reaction with a 1:2 ratio of $[\text{Li}(\text{Ph})]:[\text{Li}(\text{TMP})]$ (Scheme 1) resulted in a clear solution from which the same product crystallised upon cooling in improved yield (37%). Both triclinic ($P\bar{1}$) and monoclinic ($P2_1/n$) polymorphs have been characterised, with virtually identical molecular structures.

Compound 1 is a hexanuclear centrosymmetric complex (see Fig. 3), containing six lithium atoms in three different coordination geometries. The first environment is the $\eta^1:\eta^1\text{-Li}(1)$, which is bound to the amide nitrogen atoms of two TMP molecules. Although this is formally only two-coordinate at lithium, the flanking methyl groups of the TMP ligand must provide some degree of steric protection, as is true of the tetrameric lithium reagent $[\{\text{Li}(\text{TMP})\}_4]$,



Scheme 1. Preparation of $[\{\text{Li}(\text{TMP})\}_2\{\text{Li}(\mu\text{-Ph})\}_2]$ (1).

Identical bridging donors:



Different bridging donors:

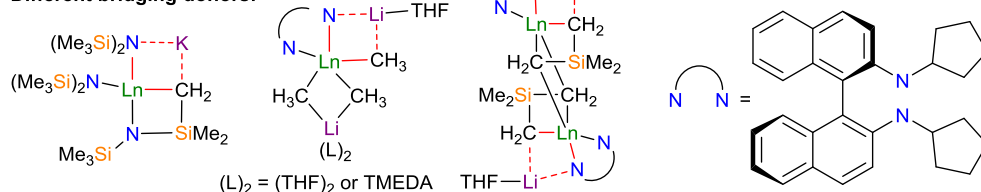


Fig. 2. Organometallic lanthanide contacted ion pairs.

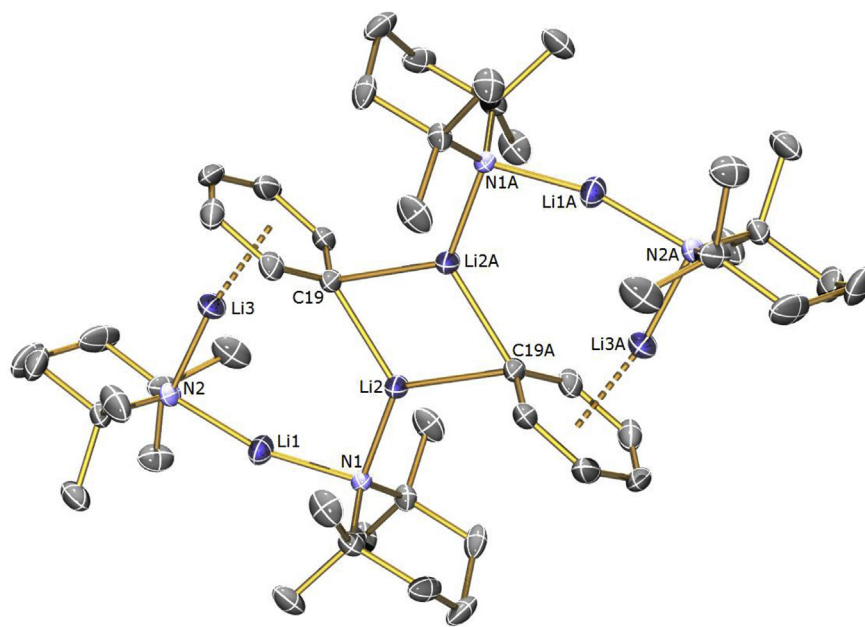


Fig. 3. Solid state structure of $[\{\text{Li}(\text{TMP})\}_2\{\text{Li}(\mu\text{-Ph})\}]_2$ (**1**). Thermal ellipsoids set at 50% probability. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles ($^\circ$) for the triclinic polymorph: Li(1)–N(1) 1.976(2), Li(1)–N(2) 1.979(2), Li(2)–N(1) 2.008(2), Li(2)–C(19) 2.217(2), Li(2)–C(19A) 2.346(2), Li(3)–N(2) 1.948(3), Li(3)–Ph_{plane} 1.944, Li(3)–C_{Ph} range 2.361(3)–2.430(3); Li(1)–N(2)–Li(3) 90.07(11), N(2)–Li(1)–N(1) 165.18(14), Li(1)–N(1)–Li(2) 99.65(10), N(1)–Li(2)–C(19) 124.50(11), N(1)–Li(2)–C(19A) 125.65(10), C(19)–Li(2)–C(19A) 109.85(9). Values for the monoclinic polymorph, all of which fall within the standard deviations of those listed above, can be found in the ESI.

which features these near linear N–Li–N motifs [39,40]. Additional electrostatic interactions with the TMP methyl groups will be tempered by their distance from the lithium centre [range of Li(1)–C_{TMP-Me} distances: 2.941–3.443 Å; cf Li(TMP) tetramer range Li–C_{TMP-Me} 2.824–3.357 Å] [40]. The second environment is the $\eta^1:\eta^1:\eta^1$ -Li(2), which is bound to one of the TMP amide nitrogen atoms and bridges between two *ipso*-carbon atoms of two phenyl rings. These Li–C interactions form a flat Li–C–Li–C core, at the midpoint of which is situated the inversion centre. This Li₂C₂ dimeric core is a signature feature of phenyl lithium structural chemistry, featuring as the repeating unit in unsolvated [Li(Ph)] [41] and as the core when solvated by (–)-sparteine [42], *N,N,N',N'*-trimethyl-1,3,5-triazacyclohexane [43], tetrahydropyran [44] and (*R,R*)-*N,N,N',N'*-tetramethyl-1,2-diaminocyclohexane [45]. The sum of the bond angles at Li(2) is 360°, indicating a trigonal planar coordination geometry for these lithium ions. The third coordination geometry is the $\eta^1:\eta^6$ -Li(3) centre which bridges a TMP amide and the π -system of the phenyl ring [46–49]. The phenyl ring is tilted with respect to the two lithium atoms coordinated to the *ipso*-carbon [angle Li(2)–C_{Ph} plane = 11.35°, Li(2A)–C_{Ph} plane = 31.80°]. This may be driven by the symmetrical η^6 -coordination of Li(3) to the phenyl π -system by enforcing all the Li(3)–C_{Ph} distances to be similar [2.361(3)–2.430(3) Å]. The TMP–Li1–TMP–Li3 unit is reminiscent of the Li(TMP) unit seen in Williard's TMEDA hemi-solvated 'open dimer' [50], or the tail of the heteroalkali-metallic complex [(PMDETA)K(μ -TMP)Li(μ -TMP)Li(TMP)] (PMDETA = *N,N,N',N',N'*-pentamethyldiethylenetriamine, Me₂NC₂H₄N(Me)₂C₂H₄NMe₂) [51]. Consequently, complex **1** can be envisaged as either a "Li(TMP) solvated" derivative of cyclic phenyl lithium or alternatively as having been formed by the insertion of phenyl lithium into the Li(TMP) tetramer. Aryl lithium insertion into the [Li(TMP)] tetramer has been witnessed previously by Klett and co-workers who inserted monomeric cyclopentadienyl lithium units into the same lithium amide [52]. Having multiple coordination geometries present for lithium within one complex has been highlighted recently by Strohmman et al. as an interesting structural feature [46], where

they presented the first complex containing both lithium– π -system contacts and lithium–carbanion interactions, so we find it pertinent to highlight the three differing lithium environments present in complex **1**.

Unfortunately, isolated crystals of **1** do not redissolve in non-polar solvents, however, samples of **1** prepared in situ in C₆D₆ were successfully analysed by ¹H and ⁷Li NMR spectroscopy. Three environments could be observed in the ⁷Li NMR spectrum (see Figure S4, ESI): the sharp signal at 2.53 ppm we attribute to Li(1), as this is a very similar chemical shift to that of [Li(TMP)]₄, wherein the lithium resides in a similar environment; a sharp signal at 1.27 ppm and a broad resonance at 0.23 ppm. The ¹H NMR spectrum features well-resolved signals in the aromatic region, and two broad resonances at lower chemical shift attributed to the H atoms of the TMP ligands.

2.2. Heterometallic species

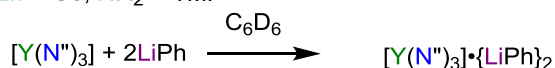
Encouraged by the preparation of the homometallic hexanuclear lithium species **1**, we then introduced rare earth amides in an attempt to prepare heterobimetallic complexes using very electropositive metals. In this initial study, we chose to investigate the reactivity of [M(CH₂Ph)] and [Li(Ph)] with [Ln(N^{''})₃] (M = Li, Na, K; Ln = Y, Ce, Nd; χ_p for Y = 1.22, Ce = 1.12, Nd = 1.14) [38] utilising the ubiquitous bis(trimethylsilyl)amide ligand, as well as [Ce(TMP)₃]. We focussed on these rare earth elements due to the reasonably interpretable NMR spectra for Ce³⁺ (4f¹) and Nd³⁺ (4f³), and in order to cover a variety of ionic radii, from Y as the smallest to Ce as the largest [53].

2.2.1. [Ln{amide}₃] + [Li(Ph)]

Firstly, we investigated the reaction of [Ln(N^{''})₃] (Ln = Ce, Nd) with [Li(Ph)] (Scheme 2). In both cases, the insoluble [Li(Ph)] instantaneously dissolves, the reaction mixtures turn black, and subsequently a substantial amount of solid material is precipitated. ¹H NMR spectroscopy of the reaction mixtures in C₆D₆ only show



Ln = Ce, Nd; R = SiMe₃
Ln = Ce; NR₂ = TMP



Scheme 2. Reactivity studies of lanthanide amides with phenyl lithium.

resonances attributable to residual $[\text{Ln}(\text{N}'')_3]$ and $[\text{Li}(\text{N}'')]$, (see ESI, Figures S5 and S6), which suggests that $[\text{Li}(\text{Ph})]$ is acting as a nucleophile, displacing $[\text{N}'']$, and has not formed a heterobimetallic species.

The parallel reactivity of $[\text{Li}(\text{Ph})]$ with diamagnetic $[\text{Y}(\text{N}'')_3]$ in a 1:1 ratio in C_6D_6 instead afforded a colourless solution, and $[\text{Li}(\text{N}'')]$ was not observed by ^1H NMR spectroscopy. Indeed, upon increasing the ratio of $[\text{Li}(\text{Ph})]$ to $[\text{Y}(\text{N}'')_3]$, the solution became pale blue at 2:1, and only in excess of this ratio did the solution darken in colour with noticeable amounts of insoluble material. As this ratio was increased to two equivalents of $[\text{Li}(\text{Ph})]$, the relative intensity of the resonance for the yttrium starting material (0.30 ppm) slowly decreased. The ^1H NMR spectrum of this new species (see Figure S7, ESI) is in agreement with this ratio as the sum of the three Ph resonances (at 8.39, 6.93 and 6.59 ppm) integrate to 10, and the N'' ligands integrate to 54, split into two singlet resonances integrating to 18 and 36 hydrogen atoms, suggesting an empirical formula of $[\text{Li}_2\text{Ph}_2\text{Y}(\text{N}'')_3]$. Using ^1H NMR DOSY, all five resonances gave the same diffusion coefficient supporting its formulation as an adduct that diffuses slower than $[\text{Y}(\text{N}'')_3]$. Unfortunately, we were unable to isolate crystals of this 2:1 reaction product to conclusively identify its structure, and therefore are unable to comment on how the Li cations are associated with the Y 'ate' complex, despite the apparent stability of this compound in solution (>2 weeks).

In light of the deleterious formation of $[\text{Li}(\text{N}'')]$ with the larger rare earth metals (6 coordinate M^{3+} ionic radii: Ce = 101, Nd = 98, Y = 90 pm) [54], we postulated that a more sterically encumbered amide could stabilise any possible adduct species that might be formed. As $[\text{Ce}(\text{TMP})_3]$ was readily prepared [55,56], we utilised this complex for reactivity studies. However, as was the case for the reaction of $[\text{Ce}(\text{N}'')_3]$ with $[\text{Li}(\text{Ph})]$, the reaction of $[\text{Ce}(\text{TMP})_3]$ with $[\text{Li}(\text{Ph})]$ afforded $[\text{Li}(\text{TMP})]$ as the only soluble product. In this case, the increased steric encumbrance slowed the rate of reaction so that the reaction was only complete after 24 h (cf $[\text{Ce}(\text{N}'')_3]$ where the reaction was instantaneous). At intermediate times, resonances due to intermediates were observed, but these could not be characterised further. At the end of the reaction, whilst we observed resonances corresponding to $[\text{Li}(\text{TMP})]$, there is also a resonance for residual $[\text{Ce}(\text{TMP})_3]$ that suggests that the reaction does not proceed in exact 1:1 stoichiometry. Ligand exchange of this type is not unknown. For instance, the preparation of $[\text{Sn}\{\text{CH}(\text{SiMe}_3)_2\}_2]$

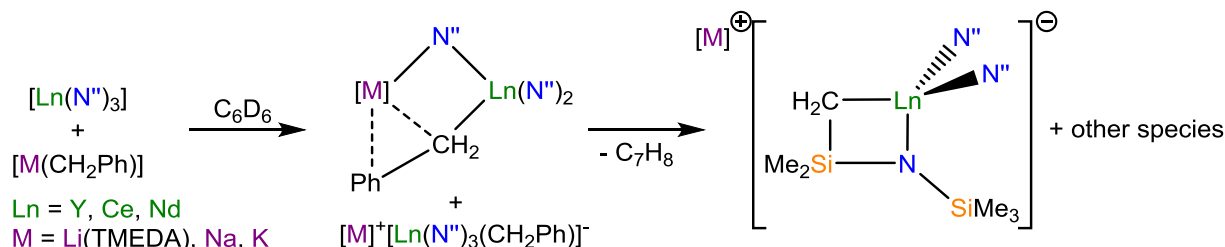
proceeds similarly by the reaction of $[\text{Li}\{\text{CH}(\text{SiMe}_3)_2\}]$ with $[\text{Sn}(\text{N}'')_2]$, which eliminates $[\text{Li}(\text{N}'')]$ [57].

2.2.2. $[\text{Ln}\{\text{amide}\}_3] + [\text{M}(\text{CH}_2\text{Ph})]$

The benzyl anion is less basic than the phenyl anion (pKa of benzene = 43, toluene = 40) [58], and we selected the readily synthesised $[\text{Na}(\text{CH}_2\text{Ph})]$ and $[\text{K}(\text{CH}_2\text{Ph})]$ for reaction studies. The lithium analogue was an oil that required the addition of one equivalent of donor ligand in order to isolate $[\text{Li}(\text{TMEDA})(\text{CH}_2\text{Ph})]$ as a solid. We started our investigations of $[\text{Ln}(\text{N}'')_3] + [\text{M}(\text{CH}_2\text{Ph})]$ with the diamagnetic yttrium complex. For all metal benzyl species, upon mixing with $[\text{Y}(\text{N}'')_3]$ in C_6D_6 the insoluble alkali metal reagents dissolve, and ^1H NMR spectroscopy suggests the formation of adduct species, of the form $[\text{M}][\text{Y}(\text{N}'')_3(\text{CH}_2\text{Ph})]$, wherein there is an interaction between the benzyl anion and the yttrium ion (Scheme 3, Fig. 4).

For the adduct generated with $[\text{K}(\text{CH}_2\text{Ph})]$, the ^1H NMR resonance attributed to the N'' ligands has shifted from 0.30 to 0.64 ppm, and there are well resolved resonances in the aromatic region that correspond to a benzyl fragment (Figure S13, ESI). Perhaps most indicative of the formation of a Y-C bond is the presence of a doublet for the CH_2 resonance at 2.22 ppm ($^2J_{\text{YH}} = 2.6$ Hz), which is attributed to the interaction of the 100% $I = \frac{1}{2}$ ^{89}Y isotope with the CH_2 of the benzyl moiety. This two-bond coupling is readily observed, as in $[\text{Y}(\text{BIPM})(\text{CH}_2\text{Ph})(\text{THF})]$ ($\text{BIPM} = \{\text{C}(\text{PPh}_2\text{NSiMe}_3)_2\}^{2-}$, $^2J_{\text{YH}} = 1.6$ Hz) [59] or $[\text{K}][\text{Y}(\text{N}'')_2\{\kappa^2\text{-CH}_2\text{Si}(\text{Me})_2\text{N}(\text{SiMe}_3)\}]$ ($^2J_{\text{YH}} = 2.6$ Hz) [30]. Similarly, for reactions with $[\text{Na}(\text{CH}_2\text{Ph})]$, adduct formation was instantaneous and the CH_2 resonance was observed as a doublet ($^2J_{\text{YH}} = 3.2$ Hz). For $\text{Li}(\text{TMEDA})$, 10 min after mixing two benzyl adducts were observed (Fig. 4), with resonances for species **a** (displaying no resolvable $^2J_{\text{YH}}$ coupling) gone within 1 h at room temperature, whereas resonances for species **b** ($^2J_{\text{YH}} = 3.4$ Hz) reduce in intensity over 2 weeks.

For all of the reactions, the adducts formed are not stable and convert to the cyclometallated product (Scheme 3), assigned by comparison of its ^1H NMR spectrum with that of the previously reported solvent free species, $[\text{K}][\text{Y}(\text{N}'')_2\{\kappa^2\text{-CH}_2\text{Si}(\text{Me})_2\text{N}(\text{SiMe}_3)\}]$ [30]. The reaction is almost complete within 1 week for K (Fig. 5) or 2 weeks for Li(TMEDA), but three species were observed by ^1H NMR spectroscopy for Na even after 2 weeks. Close inspection of ^1H NMR spectra for M = Na and K over intermediate times also revealed resonances for a second benzyl adduct, labelled **b** (Fig. 5 for M = K). For K, a CH_2 resonance was observed at 1.98 ppm ($^2J_{\text{HY}} = 3.7$ Hz) together with Ph resonances and a singlet at 0.50 ppm for N''. For Na, the CH_2 resonance for the second species was observed at 2.37 ppm ($^2J_{\text{HY}} = 4.0$ Hz). The $^1J(\text{C}-\text{H})$ coupling constant for the benzyl CH_2 group is a sensitive probe of the hybridisation of the C atom, with pyramidalised sp^3 carbanions displaying a coupling constant of approximately 125 Hz that increases to 167 Hz upon becoming planar and sp^2 hybridised [60]. Observation of the $^1J(\text{C}-\text{H})$ coupling constants in the benzyl adducts should



Scheme 3. Proposed reactivity for $[\text{Ln}(\text{N}'')_3]$ with $[\text{M}(\text{CH}_2\text{Ph})]$.

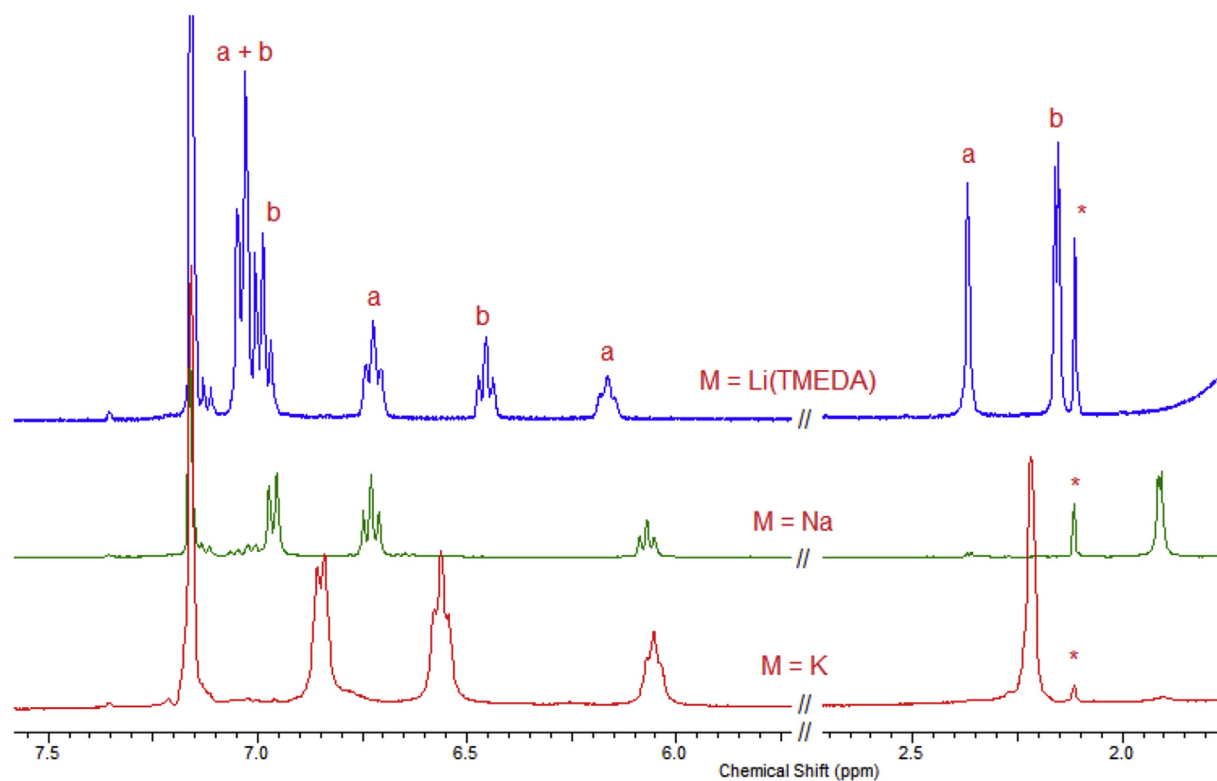


Fig. 4. Comparison of the benzylic region of the ^1H NMR spectra for the reactions of $[\text{Y}(\text{N}'')_3]$ with $[\text{M}(\text{CH}_2\text{Ph})]$ [$\text{M} = \text{Li}(\text{TMEDA}), \text{Na}, \text{K}$] 10 min after mixing. For $\text{Li}(\text{TMEDA})$, two species were observed labelled **a** and **b**. * = toluene CH_3 .

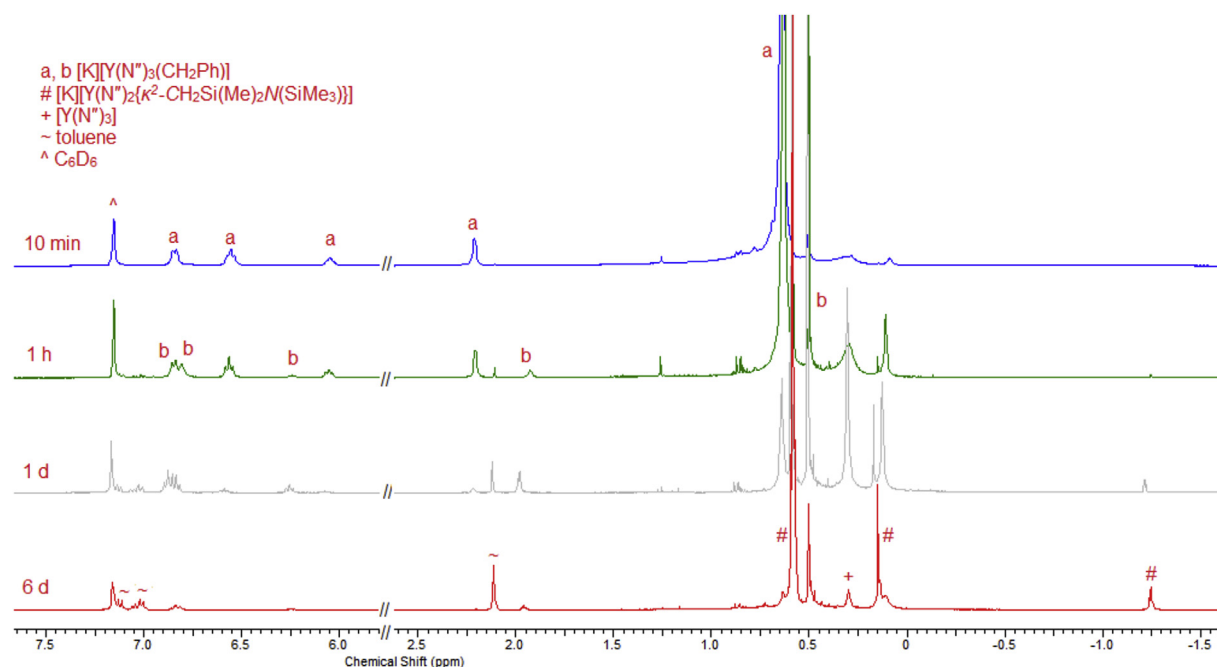
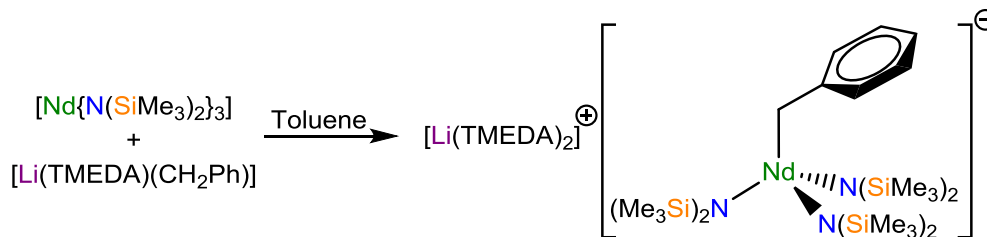


Fig. 5. Comparison of the ^1H NMR spectra for the reaction of $[\text{Y}(\text{N}'')_3]$ with $[\text{K}(\text{CH}_2\text{Ph})]$ after various time, to show ultimate conversion to $[\text{K}][\text{Y}(\text{N}'')_2(\kappa^2\text{-CH}_2\text{Si}(\text{Me})_2\text{N}(\text{SiMe}_3))]$.

therefore give more information about the hybridisation in these compounds. For $\text{M} = \text{K}$, ^{13}C satellites for the CH_2 resonances in both benzyl species were observed and gave values of 118 Hz (**a**) and 121 Hz (**b**) indicating sp^3 hybridisation. It is likely that neither of

these species is therefore a contact ion pair with a planar benzyl anion bridging the two centres. For Li , species **a** was not sufficiently stable in solution to record ^1H NMR spectra with a sufficient signal to noise ratio in order to observe the ^{13}C satellites, but species **b**



Scheme 4. Preparation of $[\text{Li}(\text{TMEDA})_2][\text{Nd}(\text{N}'')_3(\text{CH}_2\text{Ph})]$, (**2**).

displayed a ^1J coupling constant of 122 Hz, ruling out a planar benzyl anion that would be conducive for a Y-C-Li interaction, and instead suggesting a solvent separated ion pair with a pyramidalised terminal CH_2 .

The NMR spectroscopic data suggests that over time the benzyl moiety deprotonates the silyl amide ligand with the formation of a new Y-C bond. The conversion of $[\text{M}][\text{Y}(\text{N}'')_3(\text{CH}_2\text{Ph})]$ to $[\text{M}][\text{Y}(\text{N}'')_2\{\kappa^2\text{-CH}_2\text{Si}(\text{Me})_2\text{N}(\text{SiMe}_3)\}]$ for $\text{M} = \text{Na}$ is much slower than for K , whereas for $[\text{Li}(\text{TMEDA})(\text{CH}_2\text{Ph})]$, loss of the initial adduct species is fast, but the conversion to metallacycle happens over two weeks. We have been unable to definitively characterise the two different benzyl adducts, and can only tentatively propose that they might represent a contact ion pair (most likely to be species **a** for $\text{M} = \text{Li}$) and a solvent separated ion pair, as crystallographically identified for Nd (see below). The relative stability of these two species is likely to be greatly influenced by the nature of the alkali metal and the presence of TMEDA as a solvent-separating co-ligand [61].

We then turned our attention to the analogous reactivity with the f-block metals Ce and Nd . Again, the insoluble alkali metal benzyl reagents dissolved instantaneously upon mixing with $[\text{Ln}(\text{N}'')_3]$ ($\text{Ln} = \text{Ce}$ and Nd) and new resonances are observed. Fortunately, single crystals suitable for X-ray diffraction studies were grown from the reaction of $[\text{Li}(\text{TMEDA})(\text{CH}_2\text{Ph})]$ and $[\text{Nd}(\text{N}'')_3]$ after storage of a toluene solution overnight at -25°C as pale blue needles (Scheme 4), despite this adduct being the least stable (see below). The anion of **2** is shown in Fig. 6 (see Figure S2, ESI for both cation and anion).

The anion features Nd in a distorted tetrahedral geometry comprising one η^1 -benzyl and three N'' ligands. The neodymium ion sits out of the plane of the three amides by 0.62 \AA , and the sum of the three N-Nd(1)-N bond angles is 340.25° . This indicates an increase in the displacement of the Nd compared to the homoleptic precursor, $[\text{Nd}(\text{N}'')_3]$, where the sum of bond angles is 353.4° , and the Nd ion was found to be disordered 0.34 \AA above and below the plane of the three N donors [62]. Commensurate with the increased coordination number, the Nd-N bond distances have increased (av. of 2.37 \AA in **2** vs $2.29(2)\text{ \AA}$ in $[\text{Nd}(\text{N}'')_3]$) [62]. The Nd-C bond distance is slightly longer than in the homoleptic benzyl species $[\text{Nd}(\text{CH}_2\text{Ph})_3(\text{THF})_3]$ [$2.567(2)\text{ \AA}$ vs $2.601(2)\text{ \AA}$ in **2**] [13], which could reflect the increased steric bulk of the N'' groups. The carbon atom of the CH_2 unit of the benzyl moiety is also distorted away from the tetrahedral ideal $[\text{Nd}(1)\text{-C}(1)\text{-C}(2)]$ $131.5(2)^\circ$. The analogous yttrium adduct, which has a smaller ionic radius [Nd^{3+} 112.3 vs Y^{3+} 104.0 pm] [54], underwent more facile deprotonation of the silyl amide moiety, and this could be due to increased steric pressure or closer proximity in space between the benzyl and N'' ligands. The lithium cation adopts a distorted tetrahedral geometry as a consequence of the small bite angle of the tethered N_{amine} donors of the TMEDA ligands (internal N-Li-N bond angles av. 88.7°), but is otherwise unremarkable.

Due to paramagnetic effects, the resonances observed by ^1H NMR spectroscopy were broad and cover a large chemical shift range, making complete characterisation of the benzyl adducts

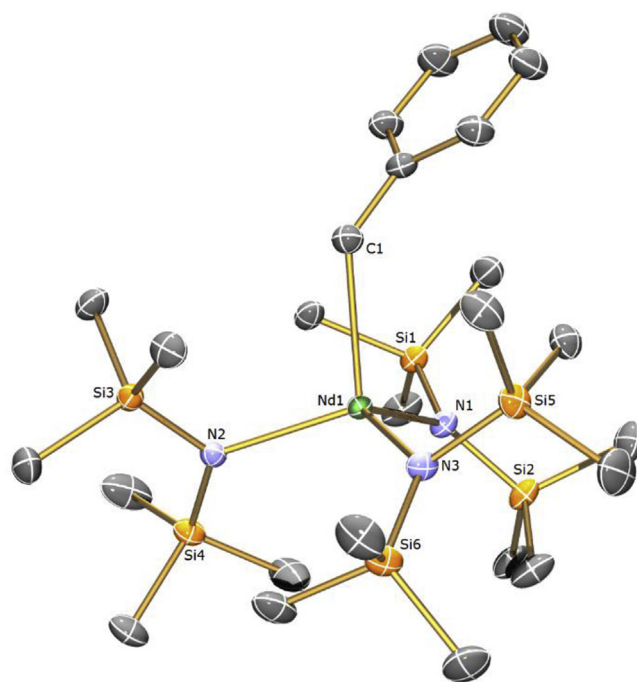


Fig. 6. Solid-state structure of the anionic moiety of $[\text{Li}(\text{TMEDA})_2][\text{Nd}(\text{N}'')_3(\text{CH}_2\text{Ph})]$, (**2**). Thermal ellipsoids set at 50% probability. Hydrogen atoms and lattice solvent (toluene) are omitted for clarity. Selected bond lengths (\AA) and angles ($^\circ$): Nd(1)-N(1) $2.3545(18)$, Nd(1)-N(2) $2.3746(18)$, Nd(1)-N(3) $2.3756(17)$, Nd(1)-C(1) $2.601(2)$; Nd(1)-C(1)-C(2) $131.5(2)$.

with Ce , Nd and the three alkali metals very difficult. For Ce , three characteristic paramagnetically shifted Ph resonances were observed directly after mixing the reagents (Figure S25, ESI), however, the CH_2 resonance could not be definitively identified. As seen for the reactions involving $[\text{Y}(\text{N}'')_3]$, these adduct complexes are not stable and undergo further reactivity with the $[\text{Li}(\text{TMEDA})]$ complex being the least stable. Inspection of the ^1H NMR spectra after several hours revealed (in all cases) resonances for both toluene and $[\text{M}(\text{N}'')]$, as well as for a new product that is assigned to be the analogous $[\text{M}][\text{Ce}(\text{N}'')_2\{\kappa^2\text{-CH}_2\text{Si}(\text{Me})_2\text{N}(\text{SiMe}_3)\}]$ cyclometallated species, data for which could be generated by waiting for the reactions to go to completion at room temperature or through heating (Figure S26, ESI).

For $[\text{Nd}(\text{N}'')_3]$, its initial reactivity with $[\text{M}(\text{CH}_2\text{Ph})]$ ($\text{M} = \text{Na}, \text{K}$) was found to follow the same pathway as for cerium and new characteristic paramagnetically shifted resonances were observed for the benzyl group, including a resonance at very low frequency (at ca. -45 ppm) assigned to the benzyl CH_2 . However, several broad resonances were observed for the N'' ligands which could not be definitively assigned to the benzyl adduct because they could not be differentiated from $[\text{Nd}(\text{N}'')_3]$ or other by-products. None of the benzyl adducts were stable and they converted to the

cyclometallated species $[M][\text{Ln}(\text{N}''')_2\{\kappa^2\text{-CH}_2\text{Si}(\text{Me})_2\text{N}(\text{SiMe}_3)\}]$ (Figure S28, ESI) with elimination of toluene over the course of several days. $[M(\text{N}'')]$ can also be observed by ^1H NMR spectroscopy, suggesting that again the mechanisms here are not straightforward.

In light of the preparation of **2**, we can then comment on the stability of benzyl species in the presence of silyl amide ligands. As has been observed in the NMR studies detailed above, it is evident that benzyl adducts are initially formed, however, deprotonation of a silyl amide ligand is relatively facile and proceeds at room temperature. This follows literature precedent for the reaction of $[\text{Y}(\text{N}'')_3]$ with $^t\text{BuLi}$ [30]. There is also a general lack of literature examples for benzyl ligands in the presence of silyl amide ligands indicating their incompatibility, with only examples of Sc, Ti, Al or Ta benzyls in the presence of N'' [36,63–65], as well as Zr or Th benzyls with tris(silylamido)amines [66,67], known.

Reactions of $[M(\text{CH}_2\text{Ph})]$ $[M = \text{Li}(\text{TMEDA}), \text{Na}, \text{K}]$ with $[\text{Ce}(\text{TMP})_3]$ in C_6D_6 were attempted. However, large amounts of solid material precipitated which we have been unable to characterise. For $M = \text{K}$ and Na , the major soluble product appears to be free tetramethylpiperidine, presumably arising from a reaction with the solvent. A stable bimetallic product was therefore not obtained.

3. Conclusion

The synthesis of bimetallic species based on very electropositive metals made through the combination of metal amides and metal phenyl or benzyl compounds was studied, and different results were obtained for lithium as opposed to group 1/rare earth mixtures. Lithium, with its greater tendency for multi-centre bonding, generated a hexametallic species with three different Li coordination environments. $[\text{Ln}(\text{N}'')_3]/\text{alkali}$ metal organometallics, with very ionic bonding, demonstrated the initial formation of 'ate' complexes by ^1H NMR spectroscopy, and $[\text{Li}(\text{TMEDA})_2][\text{Nd}(\text{N}'')_3(\text{CH}_2\text{Ph})]$ was structurally characterised. However, these adducts were not stable with respect to ligand deprotonation and formation of the cyclometallated species $[M][\text{Ln}(\text{N}'')_2\{\kappa^2\text{-CH}_2\text{Si}(\text{Me})_2\text{N}(\text{SiMe}_3)\}]$. Despite the greater resistance of the TMP anion to strong bases, no bimetallic species could be identified with $[\text{Ce}(\text{TMP})_3]$. Future work will focus on the combination of lanthanide amides with the softer organometallics of groups 2 and 12.

4. Experimental

All reactions were performed under an oxygen-free (H_2O , $\text{O}_2 < 0.5$ ppm) nitrogen atmosphere using standard Schlenk line techniques or by using an MBRAUN UNilab Plus glovebox. Anhydrous toluene was obtained from an MBRAUN SPS-800 and 40–60 petroleum ether was distilled from sodium wire; benzene and benzene- d_6 were dried over molten potassium and distilled. All anhydrous solvents were degassed before use and stored over activated molecular sieves. $\text{TMP}(\text{H})$ was dried over activated 4 Å molecular sieves, TMEDA was dried over CaH_2 and distilled, and LiN'' was sublimed prior to use. The following compounds were prepared according to literature methods: $[\text{Li}(\text{Ph})]$ [68], $[\text{Li}(\text{TMP})]$ [39], $[\text{Li}(\text{TMEDA})(\text{CH}_2\text{Ph})]$ [69], $[\text{Na}(\text{CH}_2\text{Ph})]$ [60], $[\text{K}(\text{CH}_2\text{Ph})]$ [70], $[\text{Y}(\text{N}'')_3]$ [71], $[\text{Ce}(\text{N}'')_3]$ [9,72], $[\text{Nd}(\text{N}'')_3]$ [73], and $[\text{Ce}(\text{TMP})_3]$ [55,56]. NMR spectra were recorded on Bruker AVI400 or AVIII400 spectrometers and the chemical shifts δ are noted in parts per million (ppm) calibrated to the residual proton resonances of the deuterated solvent. X-ray diffraction experiments were performed on single crystals of the samples covered in inert oil and placed under the cold stream of the diffractometer, and exposures were collected using $\text{Mo K}\alpha$ radiation ($\lambda = 0.71073$ Å). Indexing, data

collection and absorption corrections were performed and structures were solved using direct methods (SHELXT) [74] and refined by full-matrix least-squares (SHELXL) [74] interfaced with the programme OLEX2 [75] (Table S1). Diffraction experiments were carried out at Heriot-Watt University (Bruker X8 APEXII at 100 K), the University of Edinburgh (Oxford Diffraction SuperNova, Dual at 120 K) and the University of Strathclyde (Oxford Diffraction Gemini at 153 K). CCDC deposition numbers: 1568980–1568983. Elemental analyses were performed by Mr Stephen Boyer at London Metropolitan University. Although elemental analysis was repeatedly attempted, unsatisfactory results were obtained. This is an acknowledged problem with some organometallic compounds, often those containing silicon [76–78], which can lead to unsatisfactory elemental analyses. In addition, the thermal instability of these compounds added to these difficulties as well.

4.1. Preparation of $[\{\text{Li}(\text{TMP})_2\}\{\text{Li}(\text{Ph})\}]_2$ (**1**)

$[\text{Li}(\text{Ph})]$ (21.0 mg, 0.25 mmol) and $[\text{Li}(\text{TMP})]$ (73.6 mg, 0.50 mmol) were added to a 5 mL ampoule and dissolved in benzene (3 mL). The mixture was heated to 80 °C for 2 h. Upon slow cooling to room temperature, pale yellow crystals of **1** suitable for X-ray diffraction studies were grown (35 mg, 0.05 mmol, 37%). In-situ ^1H NMR (400 MHz, 25 °C, C_6D_6): δ 8.28 (4H, d, o-Ph, $^2J_{\text{HH}} = 6.4$ Hz), 7.08 (4H, t, m-Ph, $^2J_{\text{HH}} = 7.2$ Hz), 6.91 (2H, t, p-Ph, $^2J_{\text{HH}} = 7.6$ Hz), 1.70 (8H, br, TMP), 1.18 (64H, br, TMP); In-situ ^7Li NMR (155 MHz): δ 2.53 (s, N-Li-N), 1.27 (s), 0.23 ppm (br). Elemental analysis of different crystalline samples was attempted three times, but was consistently low on C.

4.2. NMR studies

Lanthanide tris(amides) $[\text{Y}(\text{N}'')_3]$, $[\text{Ce}(\text{N}'')_3]$, $[\text{Nd}(\text{N}'')_3]$ and $[\text{Ce}(\text{TMP})_3]$, were reacted on an NMR scale in a 1:1 ratio with the alkali metal reagents $[\text{Li}(\text{Ph})]$, $[\text{Li}(\text{TMEDA})(\text{CH}_2\text{Ph})]$, $[\text{Na}(\text{CH}_2\text{Ph})]$ and $[\text{K}(\text{CH}_2\text{Ph})]$, in approximately 0.5 mL of C_6D_6 . Initial spectra were taken, and then the samples were left to stand at room temperature. Further spectra were taken after appropriate time intervals (stated in the stack plots for these spectra in the ESI).

4.2.1. $[\text{Ln}(\text{N}'')_3] + [\text{Li}(\text{Ph})]$ ($\text{Ln} = \text{Ce}, \text{Nd}$)

^1H NMR (400 MHz): δ 0.14 ppm (18H, s, Me, $[\text{Li}(\text{N}'')]$) and δ -3.39 ppm (54H, s, Me, $[\text{Ce}(\text{N}'')_3]$) or -6.24 ppm (54H, s, Me, $[\text{Nd}(\text{N}'')_3]$).

4.2.2. $[\text{Y}(\text{N}'')_3] + [\text{Li}(\text{Ph})]$

$[\text{Li}]_2[\text{Y}(\text{N}'')_3(\text{Ph})_2]$ ^1H NMR (400 MHz): δ 8.39 (4H, dt, Ph, $^2J_{\text{HH}} = 7.6, 1.6$ Hz), 6.93 (4H, t, Ph, $^2J_{\text{HH}} = 7.2$ Hz), 6.59 (4H, t, Ph, $^2J_{\text{HH}} = 7.2, 2$ Hz), 0.51 (36H, s, $2 \times \text{N}''$), -0.20 ppm (18H, s, $1 \times \text{N}''$). Residual $[\text{Y}(\text{N}'')_3]$ is observed in the 1:1 reaction: δ 0.30 ppm. ^{13}C NMR (100 MHz): δ 187.84 (d, Y-C_{Ph}, $^1J_{\text{YC}} = 49$ Hz), 139.89 (s, Ph), 127.21 (s, Ph), 125.07 (s, Ph), 5.18 (s, $2 \times \text{N}''$), 5.10 ppm (s, $1 \times \text{N}''$), 4.01 ppm (s, $[\text{Y}(\text{N}'')_3]$). ^{29}Si NMR (80 MHz): δ -8.64 ($1 \times \text{N}''$), -11.52 ($2 \times \text{N}''$), -11.37 ppm (s, $[\text{Y}(\text{N}'')_3]$, $3 \times \text{N}''$). ^7Li NMR (155 MHz): δ 1.08 and -6.39 ppm. For 2D DOSY and associated diffusion rates, see ESI, Figure S11 and Table S2.

4.2.3. $[\text{Y}(\text{N}'')_3] + [\text{K}(\text{CH}_2\text{Ph})]$

$[\text{K}][\text{Y}(\text{N}'')_3(\text{CH}_2\text{Ph})]$ ^1H NMR (400 MHz): δ 6.85 (2H, d, Ph, $^2J_{\text{HH}} = 7.2$ Hz), 6.56 (2H, t, Ph, $^2J_{\text{HH}} = 6.8$ Hz), 6.05 (1H, t, Ph, $^2J_{\text{HH}} = 6.8$ Hz), 2.22 (2H, d, Y-CH₂, $^2J_{\text{YH}} = 2.6$ Hz), 0.64 ppm (54H, s, N''); ^{13}C NMR (100 MHz): δ 137.92 (s, Ph), 129.34 (s, Ph), 125.68 (s, Ph), 123.38 (s, Ph), 24.06 (d, Y-CH₂, $^1J_{\text{YC}} = 23.6$ Hz), 5.97 (s, N''). ^{29}Si NMR (80 MHz): δ -10.84 ppm.

4.2.4. $[Y(N''_3)] + [Na(CH_2Ph)]$

[Na][Y(N''₃)(CH₂Ph)] ¹H NMR (400 MHz): δ 6.96 (2H, d, Ph, ²J_{HH} = 7.6 Hz), 6.73 (2H, t, Ph, ²J_{HH} = 8 Hz), 6.07 (1H, t, Ph, ²J_{HH} = 6.8 Hz), 1.91 (2H, d, Y-CH₂, ²J_{YH} = 3.2 Hz), 0.30 ppm (54H, s, N''). Additional resonances at 0.44 and 0.01 ppm are unidentified. Selected ¹³C NMR resonances (100 MHz): 52.98 (d, Y-CH₂, ¹J_{YC} = 29.3 Hz).

4.2.5. $[Y(N''_3)] + [Li(TMEDA)(CH_2Ph)]$

[Li(TMEDA)][Y(N''₃)(CH₂Ph)] as a mixture of two benzyl species. ¹H NMR (400 MHz): δ 7.04 (2H, d, Ph, ²J_{HH} = 7.7 Hz, **a**), 6.99 (m, **b**) 6.72 (2H, t, Ph, ²J_{HH} ≈ 7 Hz, **a**), 6.46 (t, **b**), 6.16 (1H, t, Ph, ²J_{HH} ≈ 7 Hz, **a**), 2.37 (s, **a**) 2.16 (2H, d, Y-CH₂, ²J_{YH} = 3.4 Hz, **b**), 1.46 (bs, TMEDA), 0.61 (bs), 0.54 (s, N''), 0.32 (bs, N'').

4.2.6. $[Ce(N''_3)] + [K(CH_2Ph)]$

[K][Ce(N''₃)(CH₂Ph)] ¹H NMR (400 MHz): δ 11.98 (br, 2H, Ph), 6.83 (br, 2H, Ph), 4.45 (br, 1H, Ph), 0.17 (s, [K(N'')] impurity), –1 to –3 (overlapping br resonances, ca. 36H), –5.13 (br, ca. 18H). CH₂ not identified and may be obscured by the broad resonances.

[K][Ce(N''₂)(κ²-CH₂Si(Me)₂N(SiMe₃))] ¹H NMR (400 MHz): 10.03 (s, 6H, SiMe₂), 0.17 (s, [K(N'')] impurity), –3.71 (36H, s, 2 × N''), –3.77 (s, 9H, SiMe₃), –14.39 (s, 2H, CH₂). ²⁹Si NMR (80 MHz): δ 1.19, –20.60, –25.04 ppm.

4.2.7. $[Ce(N''_3)] + [Li(TMEDA)(CH_2Ph)]$

[Li(TMEDA)][Ce(N''₃)(CH₂Ph)] ¹H NMR (400 MHz): δ 14.93 (2H, br, Ph), 6.52 (2H, br, Ph), 3.92 (1H, br, Ph), 1.58–1.82 (br, 12 + 4H, TMEDA), 0.35 (s, [Li(N'')] impurity), –3.25 (br s, ca. 36H, N''), –4.97 ppm (br s, ca. 18H, N''). CH₂ not identified.

4.2.8. $[Nd(N''_3)] + [K(CH_2Ph)]$

[K][Nd(N''₃)(CH₂Ph)] ¹H NMR (400 MHz): δ 8.63 (2H, br, Ph), 6.42 (2H, br, Ph), 0.57 (br s, 54 H, N''), –3.95 (br s, [K][Nd(N''₂)(κ²-CH₂Si(Me)₂N(SiMe₃))] impurity), –6.28 (br s, [Nd(N''₃)]), –14.05 (1H, br, Ph), –45.4 ppm (2H, br, Nd-CH₂).

4.2.9. $[Nd(N''_3)] + [Na(CH_2Ph)]$

[Na][Nd(N''₃)(CH₂Ph)] ¹H NMR (400 MHz): δ 9.74 (2H, br, Ph), 6.42 (2H, br, Ph), 0.60 (54H, s, N''), –14.03 (1H, br, Ph), –44.8 ppm (2 h, br, Nd-CH₂);

[Na][Nd(N''₂)(κ²-CH₂Si(Me)₂N(SiMe₃))] δ 13.37 (6H, s, SiMe₂), –0.83 (9H, s, SiMe₃), –4.75 (36H, s, 2xN''), –12.2 ppm (2H, s, Nd-CH₂); [Nd(N''₃)] δ –6.26 ppm (54H, s, 3 × N'').

4.2.10. $[Nd(N_3)] + [Li(TMEDA)(CH_2Ph)]$

[Li(TMEDA)][Nd(N''₃)(CH₂Ph)] ¹H NMR (400 MHz): δ 8.69 (2H, br, Ph), 1.47–1.73 (br, TMEDA), –3.34 (54H, br), –34.1 ppm (2H, br, Nd-CH₂). Other resonances from the Ph group could not be definitively assigned. Some [Li(TMEDA)₂][Nd(N''₂)(κ²-CH₂Si(-Me)₂N(SiMe₃))] was also evident: δ 14.26 (6H, s, SiMe₂), 1.46–1.74 (24 + 8H, v br, 2 × TMEDA), –2.77 (9H, s, SiMe₃), –4.39 (36H, s, 2 × N''), –12.14 ppm (2H, br, Nd-CH₂).

[Li(TMEDA)][Nd(N''₂)(κ²-CH₂Si(Me)₂N(SiMe₃))] ¹H NMR (400 MHz): δ 14.40 (s, 6H, SiMe₂), –2.96 (s, 9H, SiMe₃), –4.33 (s, 36H, 2 × N''), –12.2 ppm (s, 2H, Nd-CH₂).

Single crystals of [Li(TMEDA)₂][Nd(N''₃)(CH₂Ph)] formed from the reaction mixture of [Nd(N''₃)] (56.4 mg, 0.09 mmol) and [Li(TMEDA)(CH₂Ph)] (19.2 mg, 0.09 mmol) in toluene (5 cm³) after storage in the freezer at –25 °C overnight (blue needles suitable for X-ray diffraction studies, 35 mg). NMR spectroscopy showed multiple samples to be mixtures of Li(TMEDA)₂[Nd(N''₃)(CH₂Ph)], [Li(TMEDA)][Nd(N''₂)(κ²-CH₂Si(Me)₂N(SiMe₃))] and [Nd(N''₃)] in varying proportions.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at <https://doi.org/10.1016/j.jorganchem.2017.10.022>.

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