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Review

Lanthanoid(II) tetraphenylborate complexes: From discrete ions to pseudo metallocenes☆

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Contents

Abstract

This article describes the synthetic strategies, structural features and reactivity of a unique class of discrete cationic lanthanoid(II) complexes with tetraphenylborate counter ions. In addition, variable binding of these 'weakly coordinating anions' (WCA) to the large electropositive f-element metal cations can also occur.

Keywords: Lanthanoids; Lanthanoid(II); Tetraphenylborate; Weakly coordinating anions; Rare Earths

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1. Introduction

Tetraphenylborate, BPh_4^- (Fig. 1), has been utilized in metal-based chemistry across the periodic table as a weakly coordinating anion, resulting in formation of discrete ionic metal complexes, e.g. $[M(L)_x(S)_y]^{n+}$ $[BPh_4^-]_n$. The anion is conspicuous for its lack of donor atoms, such as O, N, S, and this is of particular importance when dealing with highly oxophilic and coordinatively unsaturated lanthanoid metal centres. Other classical WCA such as ClO_4^-, BF_4^-, PF_6^-, $CF_3SO_3^-$ are less suited for organolanthanoid cations as they will either coordinate under non-aqueous conditions or will degrade the highly reactive organometallic species [1]. Furthermore, BPh_4^- has a reasonably diffuse negative charge, with theoretical calculations placing *ca.* 20% on each of the four Ph rings (Fig. 1) [2].

Thus, Coulombic attraction between the counter anion and the metal cation is reduced, increasing the propensity for charge separated ionic species. As an interesting counterpoint, BPh_4^- also has a small but fascinating coordination chemistry with some transition metals, as a consequence of the ability of these elements to form strong metal–π-arene interactions [3]. Thus, typical metal–arene complexes can be mimicked with BPh_4^- giving for example $Ph_3B(\eta^6\text{-Ph})RuCp$ [3b], and even a pseudo 'sandwich' complex, e.g. $[Nb(CO)(\eta^6\text{-Ph})_2BPh_2]$, can be formed in this fashion [3c]. Furthermore, the simple alkali metals salts $M(BPh_4)$ (M = Na, K, Cs, Rb) are polymeric in the solid state, held together by weak metal–phenyl interactions (Fig. 2) [4].

Research interest in cationic organolanthanoid(III) complexes has been fuelled by the extraordinary reactivity of cationic group 4 metal organometallics, such as Cp_2ZrR^+ species (Cp = general cyclopentadienyl anion, $C_5R_5^-$), for

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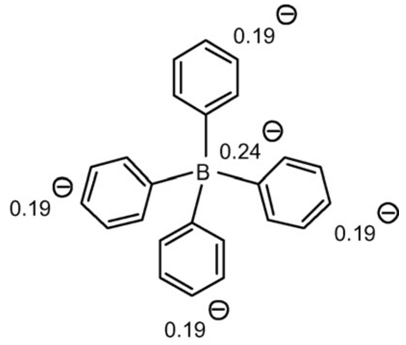

Fig. 1. Theoretical charge distribution in the BPh_4^- anion.

catalytic transformations of olefin substrates including polymerization [5]. This led to early work on the analogous actinoid complexes, particularly those of Th(IV) and U(IV) [6]. Popular counter anions for these organometallic cations are the fluorinated tetraphenylborates, $B(C_6F_5)_4^-$ and related derivatives, or alternatively, $B(C_6F_5)_3R^-$ derived from abstraction of one R group from a Cp_2MR_2 precursor by the borane, $B(C_6F_5)_3$ [5b]. The synthesis of cationic organolanthanoid(III) complexes has presented particular challenges, not the least being the dearth of dialkyl precursor complexes, e.g. $Ln(L)R_2$ [7], analogous to the readily available Cp_2ZrR_2. In addition, heteroleptic lanthanoid organometallics readily undergo ligand redistribution reactions making the synthesis of a $Ln(L)R_2$ or $Ln(L)R^+$ species by classical metathesis reaction quite challenging. Whilst early research on lanthanoid(III) tetraphenylborates was restricted to more stable systems [8], recent results have given rise to a fascinating array of isolable organolanthanoid(III) cations [9], and such species have shown exciting reactivity in catalytic polymerization, for example, with butadiene, isoprene, styrene and ethylene [10]. In most cases the BAr_4^- anion is an isolated counter-ion, but early work by Schaverien suggested BPh_4^- coordination to La in $[Cp^*La\{CH(SiMe_3)_2\}BPh_4]$ $Cp^* = C_5Me_5^-$) can occur [11]. Subsequently, Evans et al. have published the crystal structure of $[Cp^*_2Sm(\eta^2\text{-}Ph)_2BPh_2]$ which has two η^2-Ph–Sm interactions [12]. Lanthanoid cations do not readily form arene complexes [13], and thus this bonding was highly unusual and possibly quite weak.

Research in lanthanoid(II) cations has been limited by comparison with the lanthanoid(III) systems, the first example involving a crown ether induced Cp''^- ($Cp'' = C_5H_3\text{-}1,3\text{-}(SiMe_3)_2$) displacement yielding $[Cp''Sm(18\text{-cr-}6)][Cp'']$ from $SmCp''_2$ [14]. Similar methodology has recently been utilized to prepare a unique $[Ln_2(CCR)_2(S)_n]^{2+}$ dication with $CpPh_5^-$ counter ions ($CpPh_5^- = C_5Ph_5^-$) [15]. Considering that 'unbound' Cp anions are unlikely to be widely suitable as counterions for organolanthanoid(II) cations (due to facile protonation giving CpH), we investigated the use of BPh_4^- as a simple alternative. This article reviews the synthesis and structural characterization of cationic organolanthanoid(II) complexes having discrete tetraphenylborate counter ions [16], as well as systems where associated coordinated solvent molecules are restricted leading to tetraphenylborate coordination to the lanthanoid(II) cation, via unusual π-arene-lanthanoid structures [17].

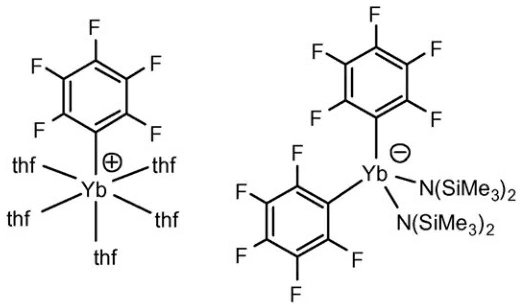

Fig. 3. The 'rogue' structure containing the $[Yb(C_6F_5)(thf)_5]^+$ cation.

2. Synthesis of discrete ion pairs

2.1. Aryllanthanoid(II) cations

Our interest in organolanthanoid(II) cations arose from the observation of such a highly unusual species in a 'rogue' crystal structure, *viz.* mixed-valent $[Yb^{II}(C_6F_5)(thf)_5][Yb^{III}(C_6F_5)_2\{N(SiMe_3)_2\}_2]$ (Fig. 3).

This remarkable complex was isolated in low yield from an attempt to prepare an unsymmetrical ytterbium(II) organoamidoorganometallic $Yb(C_6F_5)\{N(SiMe_3)_2\}$ and is likely to be a serendipitous result of decomposition of the target compound and subsequent ligand redistribution and oxidation [16]. Following the synthetic methodology used to prepare $[Yb(C_6F_5)(L)]$ complexes (e.g. $L = Cp^*$) [18], a pure sample of $[Yb(C_6F_5)(thf)_5][BPh_4]$ was isolated in high yield from selective protolysis of '$Yb(C_6F_5)Ph$' (prepared *in situ* from Yb and $Hg(C_6F_5)Ph$) by Me_3NHBPh_4 in thf (Fig. 4) [16].

$$\begin{aligned} &Ln + Hg(C_6F_5)Ph + Me_3NHBPh_4 \\ &\quad \rightarrow [Ln(C_6F_5)(thf)_n][BPh_4] + Hg + PhH + NMe_3 \end{aligned}$$

The analogous Eu(II) species $[Eu(C_6F_5)(thf)_6][BPh_4]$ was also prepared, but, for Sm(II) facile decomposition occurred and the only lanthanoid species detected was the known fully solvated dication $[Sm(thf)_7][BPh_4]_2$,[19] which was converted to a MeCN complex for isolation [20]. Similarly, an attempt to prepare a PhCC analogue, $[Yb(CCPh)(thf)_n][BPh_4]$ by reaction of Yb, HgPh(CCPh) and Me_3NHBPh_4, gave $[Yb(thf)_6][BPh_4]_2$

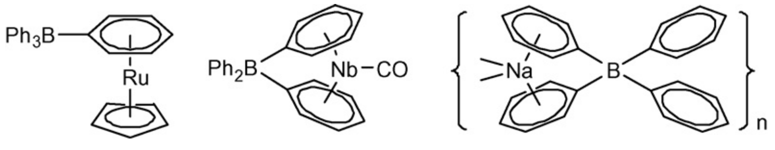

Fig. 2. Examples of transition metal complexes with 'coordinated' BPh_4^-, and the alkali metal salts.

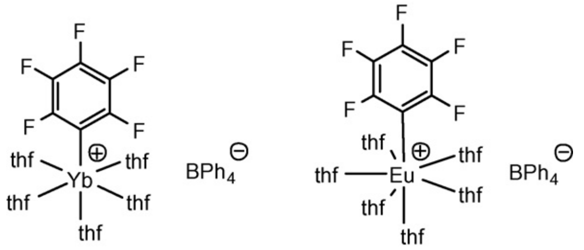

Fig. 4. Synthesis of $[Ln(C_6F_5)(thf)_n][BPh_4]$, Ln = Eu, $n = 6$; Ln = Yb, $n = 5$.

[20]. Despite the instability of the putative Sm(II) analogue, the $[Ln(C_6F_5)(thf)_n]^+$ cations (Ln = Eu, Yb) were remarkably thermally robust, by comparison with the neutral $[Ln(C_6F_5)_2(thf)_n]$ counterparts, which decompose readily after 24–48 h at room temperature [21]. Both tetraphenylborate complexes were characterized by elemental analyses, spectroscopic methods and X-ray structure determinations [16]. The observed increase in coordination number from Yb (octahedral) to Eu (pentagonal bipyramid) is as expected based on the larger ionic radius of the latter. A unique spectroscopic feature of $[Yb(C_6F_5)(thf)_5][BPh_4]$ was the first observation of ^{171}Yb–^{19}F coupling in the ^{171}Yb NMR. At RT, a single broad peak is observed at $\delta = 304$ ppm, which lies between those of $[Yb(C_6F_5)_2(thf)_4]$ (463 ppm) and $[Yb(thf)_6]$ $[Ce(COT)_2]$ (256 ppm) and confirms the integrity of the cation in solution. Upon lowering the temperature to 243 K, a moderately well defined triplet of triplets was resolved, with coupling constants of 48 and 33 Hz for the *ortho*- and *meta*-fluorine nuclei, respectively (Fig. 5). This prompted us to re-examine the ^{171}Yb NMR spectrum of $[Yb(C_6F_5)_2(thf)_4]$ at low temperatures (233 K) which led to a 17 line spectrum, with $^3J_{YbF}$ 39 Hz and $^4J_{YbF}$ 13 Hz [16].

The crystal structures of the $[Ln(C_6F_5)(thf)_n]^+$ cations (Ln = Eu, Yb) showed significantly shorter Ln–C bonds than for the neutral complexes $[Ln(C_6F_5)_2(thf)_n]$ [16]. The latter were considered to be long, as a result of the *trans* disposition of the two anions, whereas the current distances are more typical of σ-Ln^{II}-aryl bonds. Studies of the thermal behaviour of $[Ln(C_6F_5)_2(thf)_n]$ (Ln = Eu, Yb) suggested that these decompose primarily by SET/fluoride abstraction pathways [21]. The positive charge on the $[Ln(C_6F_5)(thf)_n]^+$ cations would inhibit electron transfer from the metal to the fluorine and this may account for their observed stability. Deliberate thermal decomposition of $[Yb(C_6F_5)(thf)_5][BPh_4]$ in C_6D_6 gave $[Yb(thf)_6][BPh_4]_2$ and organic fragments consistent with homolytic cleavage of the Yb–C bond rather than C–F activation despite the stronger Yb–C bond. This is consistent with deactivation of the fluoride abstraction pathway in the cationic complexes.

2.2. Fully solvated lanthanoid(II) cations

The isolation of bulk quantities of the $[Ln(C_6F_5)(thf)_n]^+$ cations (Ln = Eu, Yb) and the extensive synthetic chemistry displayed by their neutral counter parts [22] prompted us to investigate their reactivity. Thus, ligand exchange reactions of $[Yb(C_6F_5)(thf)_5][BPh_4]$ with protic reagents ArOH ($Ar = C_6H_2$-2,6-$Bu_2{}^t$-4-Me, R_2pzH ($R_2pz = C_3HN_2$-3,5-Bu^t), and RH (R = PhCC) and indene were attempted (Fig. 6) [20]. The results were singularly disappointing with the precipitation of $[Yb(thf)_6][BPh_4]_2$ observed in all cases, along with concomitant formation of the respective $Yb(L)_2$ species. This behaviour was consistent with previous observations of Evans

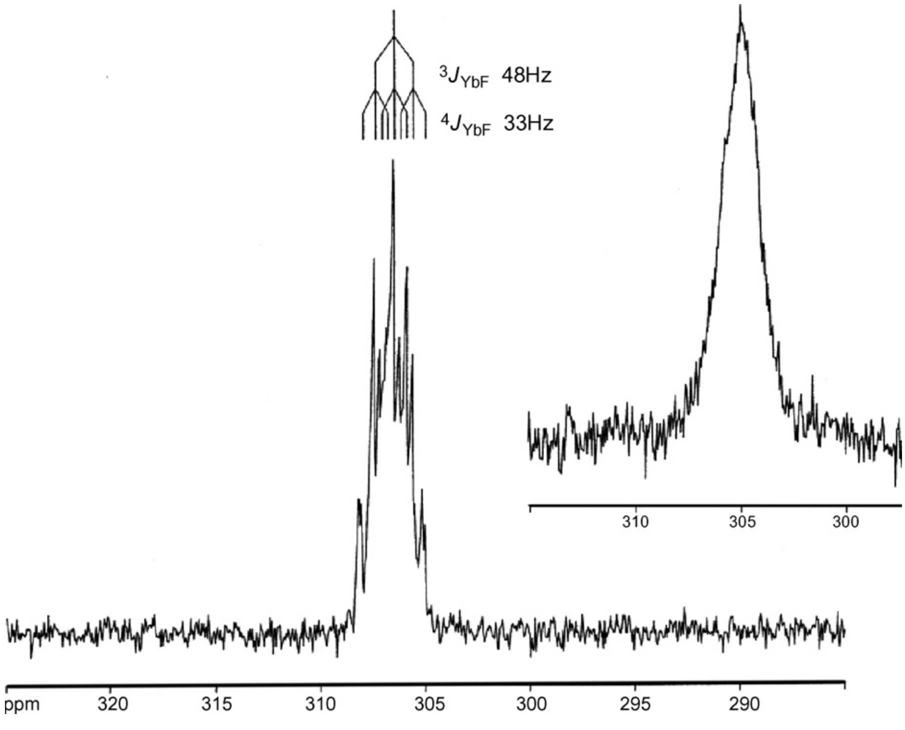

Fig. 5. Low temperature ^{171}Yb NMR spectrum of $[Yb(C_6F_5(thf)_5][BPh_4]$ showing ^{171}Yb–^{19}F coupling (RT spectrum inset) (©reproduced with permission from Wiley–VCH).

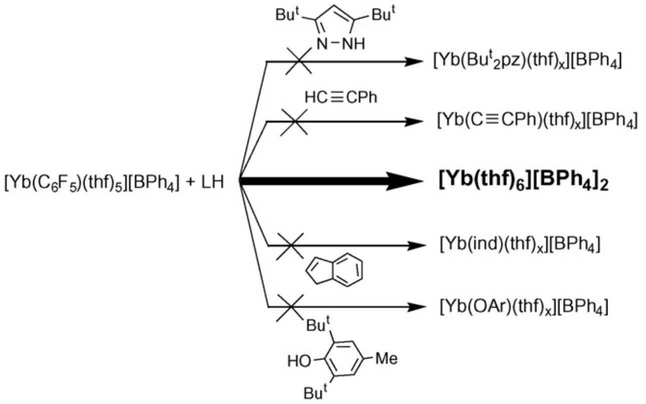

Fig. 6. Attempted reactions of $[Yb(C_6F_5(thf)_5][BPh_4]$.

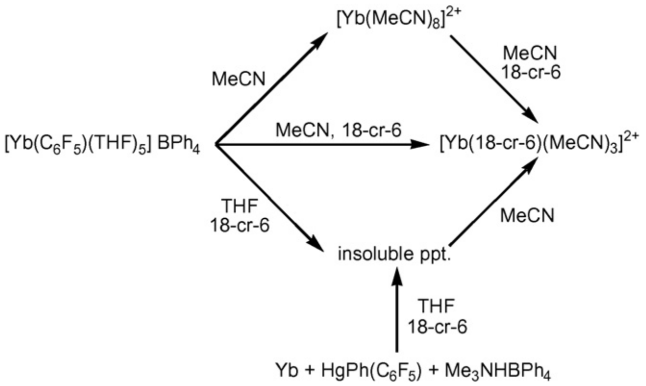

Fig. 7. Syntheses of $[Yb(18\text{-cr-}6)(S)_n][BPh_4]_2$ complexes.

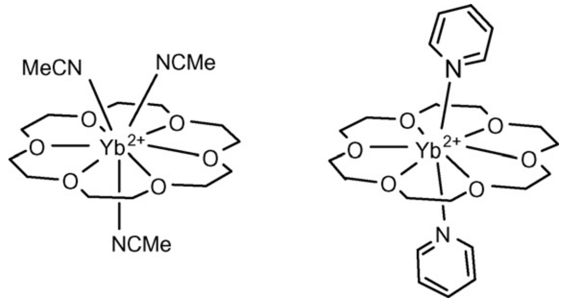

Fig. 8. Complex cations of $[Yb(18\text{-cr-}6)(NCMe)_3][BPh_4]_2$ and $[Yb(18\text{-cr-}6)(py)_2][BPh_4]_2$.

who also isolated solely the $[Ln(thf)_n][BPh_4]_2$ (Ln = Yb, Sm) species from various attempts to prepare $[Ln(L)(thf)_n][BPh_4]_2$ (L = Cp*, $N(SiMe_3)_2$) [19].

Mindful of the use of face-capping crown ethers to stabilize organolanthanoid(III) cations by Okuda and co-workers [9a,c,g,i], we studied the reactions of $[Yb(C_6F_5)(thf)_5][BPh_4]$ with 18-cr-6 (Fig. 7) in an attempt to obtain a suitable reagent for further reactivity studies. Again, ligand rearrangement/decomposition reactions predominated and gave the insoluble, fully solvated cations $[Yb(18\text{-cr-}6)(thf)_n][BPh_4]_2$ in thf [23]. Recrystallization of the products from MeCN, or utilizing MeCN as solvent, allowed isolation of crystalline $[Yb(18\text{-cr-}6)(MeCN)_3][BPh_4]_2$ with the crown ether. Given these results, it is not surprising that a similar attempt to isolate a stable $Yb(CCPh)^+$ cation, by reaction of $Yb(CCPh)_2$, Me_3NHBPh_4 and 18-cr-6 in thf gave insoluble $[Yb(18\text{-cr-}6)(thf)_n][BPh_4]_2$, which, when crystallized from py, was converted to $[Yb(18\text{-cr-}6)(py)_2][BPh_4]_2$ [23].

The structures of the crown ether complexes $[Yb(18\text{-cr-}6)(NCMe)_3][BPh_4]_2$ and $[Yb(18\text{-cr-}6)(py)_2][BPh_4]_2$ both have the crown ether in an equatorial position with the MeCN or py ligands axial (Fig. 8). However, with the smaller MeCN ligand, there is sufficient space for two coordinated molecules spanning the one axial position giving a higher coordination number for this complex. The unequal distribution of MeCN ligands is accommodated by flexing of the crown ether lariat [23].

An intriguing feature of the tetraphenylborate structures appears in the 3D packing of these complex cations and large anions. When viewed as point charges located at the Yb and B sites, respectively, the complexes form a fluorite-type lattice (Fig. 9) with an approximately cubic array of anions and a dication in the centre of alternate cubes. Thus, the cations are completely shielded by the phenyl rings. These complexes fall into the "ions in a box" description put forward by Harder et al. [24] for several group 2 and lanthanoid complex salts. Typically these have large planar delocalized carbon-based anions that occupy the sides of the boxes. However, in the BPh_4^- complexes, each B atom is located at the corner of the box with three phenyl rings lying along the adjoining faces (Fig. 9). The remaining Ph ring protrudes into the neighbouring cube in which there is no $[Yb(S)_n]^{2+}$ cation.

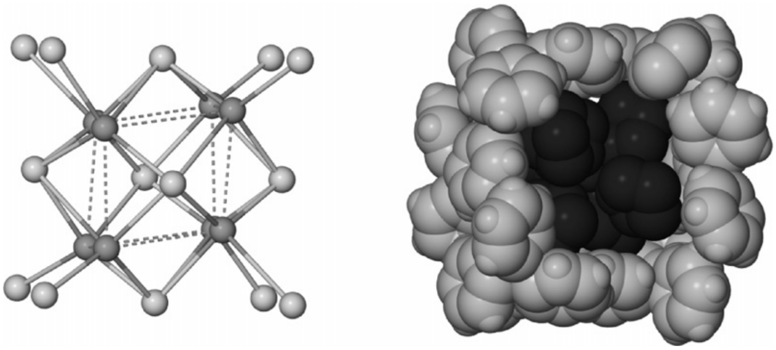

Fig. 9. Fluorite (CaF_2)type lattice of cations (light grey) and anions (dark grey) in $[Yb(S)_n][BPh_4]_2$ (lines between cations and anions are illustrative only) and space filling representation showing the cation (dark) 'in a box' of phenyl rings (light), with one corner removed.

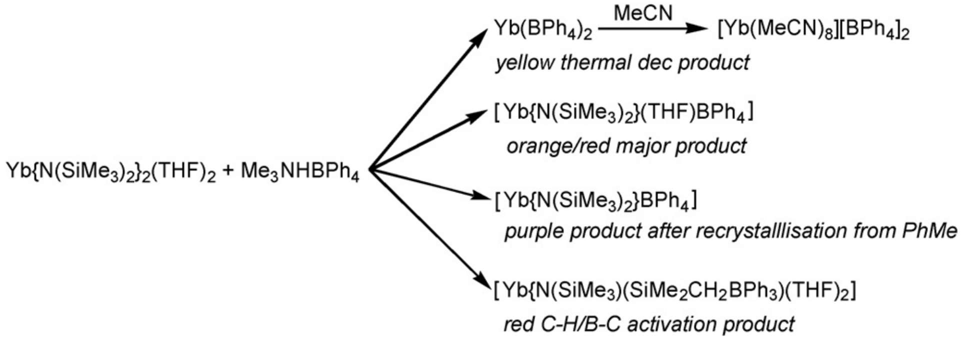

Fig. 10. Reactions of $[Yb\{N(SiMe)_2\}_2(THF)_2]$ with Me_3NHBP_4 (1:1) in PhMe.

3. Lanthanoid(II) complexes with bound tetraphenylborate

Apart from the inimitable isolation of the organolanthanoid(II) cations $[Ln(C_6F_5)(thf)_n][BPh_4]$, the presence of donor solvents or co-ligands was clearly detrimental to stabilization of unsymmetrical $[Yb(L)(S)_n][BPh_4]$ species. Consequently, the use of hydrocarbon solvents such as PhMe and hexane was pursued, but this necessitated a change in the anionic co-ligand from $C_6F_5^-$ to $(SiMe_3)_2N^-$ ($[Yb(C_6F_5)(thf)_5][BPh_4]$ decomposed instantaneously when dissolution in PhMe was attempted!) [20]. The $N(SiMe_3)_2^-$ ligand is well known in lanthanoid(II) chemistry and its complexes are readily soluble in hydrocarbons. It is a key reagent for the synthesis of other $Ln(L)_2$ complexes and can potentially react with AlR_3 compounds to produce catalytically active species (for example for ethylene polymerization) [25].

The reaction of $[Yb\{N(SiMe_3)_2\}_2(thf)_2]$ with Me_3NHBPh_4 in PhMe is quite complex, yielding a variety of products depending upon the reaction conditions (Fig. 10).

Initially, this reaction was performed at room temperature and gave, after work up in PhMe/hexane, a low yield (<10%) of the complex $[Yb\{N(SiMe_3)_2\}(thf)(BPh_4)]$ as red-orange crystals, mixed with some unreacted $[Yb\{N(SiMe_3)_2\}_2(thf)_2]$ [17a]. This result contrasts that of the identical reaction but with thf as solvent which yielded $[Yb(thf)_6][BPh_4]_2$ [19]. The $[Yb\{N(SiMe_3)_2\}(thf)(BPh_4)]$ product was identified solely by an X-ray structure determination that revealed a molecular complex with the ytterbium atom bound (via N) to a $(SiMe_3)_2N^-$ anion, to a coordinated thf ligand and to two of the phenyl rings of the BPh_4^- anion (Fig. 11). The latter are bound by the faces of the phenyl rings (ie in a π-arene fashion) as defined by the angle θ (av. Yb-cent-C(ipso); cent = centroid of interacting C atoms) of 90.0° and 90.4° for each Ph group. There is also a corresponding contraction (8.7°) of the C–B–C angle for the two interacting Ph groups. The two bound Ph rings have slightly differing η^6 and η^4 coordination modes defining a coordination number of 7 based upon Yb–C bond distances [17a]. The η^6-Ph ring has Yb–C in the narrow range 2.833(3)–2.919(3) Å whereas the η^4-Ph ring has significantly 'slipped' with a wider bonding Yb–C range 2.871(3)–3.128(3) Å and two even longer distances 3.243(3) and 3.297(3) Å considered non-bonding.

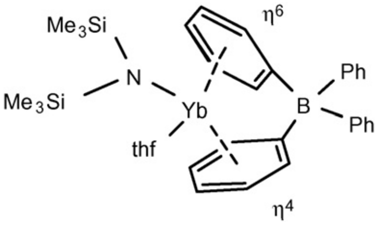

Fig. 11. One structural form of $[Yb\{N(SiMe_3)_2\}(thf)(BPh_4)]$.

Whilst these Yb–C bonds are longer than for a classical carbocyclic anion bound to a lanthanoid, e.g. 2.694(5)–2.744(5) Å in the seven coordinate cyclopentadienyl-ytterbium(II) complex $[Cp^*Yb(C_6F_5)(thf)_3]$ [18], the structural architecture bears a striking resemblance to that of a lanthanoid(III) metallocene, e.g. $Cp_2LnX(S)$ [7]. Given that the BPh_4^- is comparatively weakly bound, an associated shortening of the Yb–N bond could be anticipated and is indeed observed [17a]. This suggests that the ytterbium(II) centre may be highly Lewis acidic and a potentially reactive site.

The encouraging formation and structure of $[Yb\{N(SiMe_3)_2\}(thf)(BPh_4)]$ prompted an attempt to drive the initial reaction to completion by heating at 60 °C. In this case a yellow precipitate formed along with a red solution. IR analysis of the yellow solid suggested the presence of the BPh_4 anion but no distinctive absorptions of the $(SiMe_3)_2N^-$ ligand were apparent. Thus, formation of the thermal decomposition product $[Yb(BPh_4)_2]$ was indicated and indeed recrystallization of the yellow solid from MeCN gave the known solvent separated ion pair $[Yb(NCMe)_8][BPh_4]_2$ [17b]. Despite this considerable decomposition, concentration of the red PhMe filtrate from this reaction gave red-orange crystals of the desired product $[Yb\{N(SiMe_3)_2\}(thf)(BPh_4)]$ in reasonable yield, allowing full spectroscopic and analytical characterization. Surprisingly, an attempt to confirm the product by X-ray crystallography revealed a different structural isomer to that observed above. In this form, the BPh_4^- is bound in an η^6, η^1 fashion, with the η^6-Ph having Yb–C in the narrow range 2.802(4)–2.907(4) Å, but the latter, although bound nearly perpendicular to the plane of the Ph ring (θ = 101.1°), having only one short Yb–C of 2.763(3) Å, the remainder being >3.2 Å. Accompanying the change in Ph coordination, there is a widening of the N–Yb–O angle and the

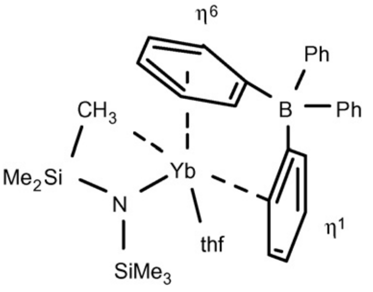

Fig. 12. Second structural form of $[Yb\{N(SMe_3)_2\}(thf)(BPh_4)]$.

presence of an agostic Yb···Me interaction (3.123(4) Å) (from the $SiMe_3$ group) (Fig. 12) [17a].

With a now acceptable (if not ideal) synthesis of $[Yb\{N(SiMe_3)_2\}(thf)(BPh_4)]$ in hand we then set out to prepare bulk quantities of this reagent for further reactivity studies. However, there were still several surprises lurking within this system. Often the product isolated from the PhMe solution was impure as indicated by the presence of a number of $SiMe_3$ signals in the NMR spectra (see also below). This necessitated further recrystallizations from PhMe, during which the colour of the solution and the product changed from red to purple. Spectroscopic analysis of the purple material suggested a new product, probably a solvent free derivative [17b]. This was confirmed by a X-ray crystallography that established the structure of $[Yb\{N(SiMe_3)_2\}BPh_4]$. By comparison with $[Yb\{N(SiMe_3)_2\}(thf)(BPh_4)]$ (see above), the purple complex has accommodated the loss of the thf ligand through an increase in the degree of Ph coordination from the BPh_4^- group. Thus, two Ph rings are bound to the ytterbium centre, *both* now with distinctly η^6-binding modes, as shown by the Yb–C ranges for both rings, e.g. 2.784(11)–2.899(11) and 2.810(7)–2.956(12) Å. In addition, there is also an agostic Yb···Me interaction from one of the $SiMe_3$ groups (Fig. 13) [17b].

Comparison of the BPh_4^- bonding in the current structure with a transition metal equivalent, e.g. $[Nb(CO)(\eta^6\text{-}Ph)_2BPh_2]$, [3c] shows longer M–C distances and considerably more acute centroid-M-centroid angles (114.0° for Yb *cf.* 131.6° for Nb) consistent with the much larger ionic radius of the lanthanoid and the ionic nature of the bonding. The current structure mimics a lanthanoid(III) *ansa*-metallocene and comparison of the respective Ln–N bond distances (after adjustment for differences in ionic radii) (Table 1) shows longer values for the lanthanoid(III) metallocenes, consistent with comparatively weaker binding of $Ln(\mu\text{-}Ph)_2BPh_2$ than $LnCp_2$ ligation.

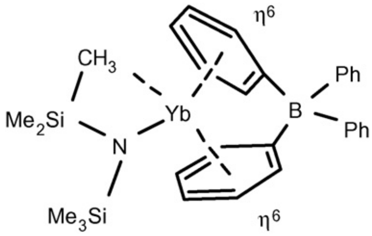

Fig. 13. Structural form of $[Yb\{N(SiMe_3)_2\}(BPh_4)]$.

Table 1

Comparison $Ln^{II}\text{-}(\eta^6\text{-}Ph)_2BPh_2$ vs. $Ln^{III}\text{-}(\eta^5\text{-}Cp)_2$ ligation on the Ln–N distances of selected $[Ln(L)N(SiMe_3)_2]$ complexes

	Ln–N (Å)	IR (Å)[a]	Ln–N–IR (Å)
$[Yb\{N(SiMe_3)_2\}BPh_4]$	2.262	1.08	1.182
$[SmCp^*_2\{N(SiMe_3)_2\}]$[b]	2.301	1.02	1.281
$[SmCp^A{}_2\{N(SiMe_3)_2\}]$[c]	2.330	1.02	1.310
$[YbCp^B{}_2\{N(SiMe_3)_2\}]$[d]	2.206	0.925	1.281
$[(fl)C(Ph)_2CpLu\{N(SiMe_3)_2]$[e]	2.196	0.919	1.277
$[\{ind(CH_2CH_2)ind\}Yb\{N(SiMe_3)_2\}]$[f]	2.168, 2.175	0.925	1.243, 1.250

$Cp^A = C_5H_4CH_2CH_2CH{=}CH_2^-$, $Cp^B = C_5H_4B(NPr_2{}^i)(NHBu^t)^-$.

[a] Ref. [31].

[b] Ref. [32].

[c] Ref. [33].

[d] Ref. [34].

[e] Ref. [35].

[f] Ref. [36].

Given the variety of Yb–Ph binding modes observed in the solid state structures of the $[Yb\{N(SiMe_3)_2\}(thf)_n(BPh_4)]$ ($n = 1$ or 0) complexes, their solution behaviour is noteworthy. As shown by the single aromatic NMR signals, the $Yb\text{–}BPh_4$ moiety is fluxional, but the observed chemical shift is indicative of coordinated BPh_4^- ligands, rather than discrete BPh_4^- ions. Thus, rapid exchange of free and bound Ph rings occurs whilst maintaining the integrity of the $Yb\text{–}BPh_4$ unit as a whole. Ultimately a modified synthesis of $[Yb\{N(SiMe_3)_2\}BPh_4]$ was devised (performing the initial reaction at *low temperature*, followed by several extraction cycles with PhMe) and the pure purple compound could be isolated in good yield [17b].

During our attempts to purify the bulk $[Yb\{N(SiMe_3)_2\}(thf)(BPh_4)]$ and prior to the discovery of the purple solvent free complex, we inadvertently isolated red crystals in small yield of one of the 'impurities' [17a]. The NMR spectrum of this complex displayed intriguing features including two sharp $SiMe_x$ resonances, one significantly shifted to higher frequencies. An X-ray structure determination enabled identification of $[Yb\{N(SiMe_3)SiMe_2CH_2BPh_3\}(thf)_2]$, an exciting C–H/B–C activation product containing an unusual amidoborate $N(SiMe_3)(SiMe_2CH_2BPh_3)^{2-}$ ligand (Fig. 14).

In this complex, the ytterbium atom is bound to the amidoborate ligand through the amide nitrogen atom and two η^2-Ph interactions, and two thf molecules giving a coordination num-

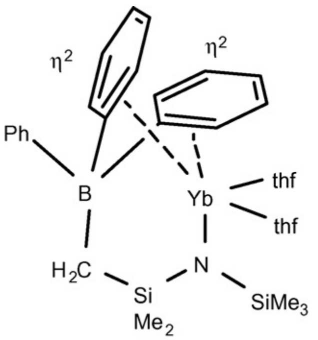

Fig. 14. C–H/B–C activation product.

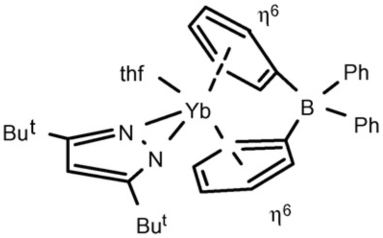

Fig. 15. Structural form of $[\mathrm{Yb}(\mathrm{Bu}^t{}_2\mathrm{pz})(\mathrm{thf})(\mathrm{Bph}_4)]$.

ber of five. The Yb–C distance range 2.635(3)–2.914(3) Å, at the shorter extreme, is close to that of a bridging $(\eta^1\eta^1)$:*phenyl anion* (e.g. in $[\mathrm{YbPh}_2(\mathrm{thf})(\mu\text{-Ph})_3\mathrm{Yb}(\mathrm{thf})_3]$ (range 2.48(3)–2.75(4) Å) [26]. An analogous amido-borate ligand has been previously observed in actinoid chemistry with the isolation of $[\mathrm{U}\{\mathrm{N}(\mathrm{SiMe}_3)_2\}_2\{\mathrm{N}(\mathrm{SiMe}_3)(\mathrm{SiMe}_3(\mathrm{CH}_2\mathrm{B}(\mathrm{C}_6\mathrm{F}_5)_3)\}]$ [27]. This was formed by reaction of $[\mathrm{U}\{\mathrm{N}(\mathrm{SiMe}_3)_2\}_3\mathrm{H}]$ with $\mathrm{B}(\mathrm{C}_6\mathrm{F}_5)_3$ and plausibly results from deprotonation of a methyl group on the $(\mathrm{SiMe}_3)_2\mathrm{N}^-$ ligand by the hydride and subsequent capture of the carbanion by the strongly Lewis acidic $\mathrm{B}(\mathrm{C}_6\mathrm{F}_5)_3$. A similar Si–C–H deprotonation/cyclization reaction has been observed with $[\mathrm{Ln}\{\mathrm{N}(\mathrm{SiMe}_3)_2\}_3]$ and $\mathrm{NaN}(\mathrm{SiMe}_3)_2$, generating in this case a Ln–CH_2–Si moiety [28]. Thermally induced nucleophilic substitution at a saturated boron by PhCC^- has been observed for $[\mathrm{Sm}\{\mathrm{HB}(\mathrm{Me}_2\mathrm{pz})_3\}_2(\mathrm{L})]$, eliminating the $\mathrm{Me}_2\mathrm{pz}^-$ anion and forming a Sm-$\{\mathrm{HB}(\mathrm{Me}_2\mathrm{pz})_2(\mathrm{CCPh})\}$ moiety [29]. In the current system, the absence of a strong base, or a suitable leaving group on the boron, suggests that $\mathrm{Yb}^{\mathrm{II}}$ induced C–H and B–C activation occurs.

Encouraged by the successful syntheses of $[\mathrm{Yb}\{\mathrm{N}(\mathrm{SiMe}_3)_2\}(\mathrm{thf})\mathrm{BPh}_4]$ and $[\mathrm{Yb}\{\mathrm{N}(\mathrm{SiMe}_3)_2\}\mathrm{BPh}_4]$, but mindful of the failure of $[\mathrm{Yb}(\mathrm{C}_6\mathrm{F}_5)(\mathrm{thf})_5][\mathrm{BPh}_4]$ as a reagent (see above), some simple reactions with protic substrates were initially attempted. When $[\mathrm{Yb}\{\mathrm{N}(\mathrm{SiMe}_3)_2\}(\mathrm{thf})\mathrm{BPh}_4]$ was treated with $\mathrm{Bu}^t{}_2\mathrm{pzH}$ in PhMe, red crystals of the pyrazolate complex $[\mathrm{Yb}(\mathrm{Bu}^t{}_2\mathrm{pz})(\mathrm{thf})\mathrm{BPh}_4]$ were readily isolated [17b]. In this complex, an η^2-bound $\mathrm{Bu}^t{}_2\mathrm{pz}$-pyrazolate has replaced the $(\mathrm{SiMe}_3)_2\mathrm{N}^-$ ligand but the smaller size of the $\mathrm{Bu}^t{}_2\mathrm{pz}^-$ ligand is accommodated by an increase in the coordination of the phenyl groups (Fig. 15).

Thus, in one form of $[\mathrm{Yb}\{\mathrm{N}(\mathrm{SiMe}_3)_2\}(\mathrm{thf})\mathrm{BPh}_4]$ the BPh_4^- is bound $\eta^6{:}\eta^4$ whereas in the $\mathrm{Bu}^t{}_2\mathrm{pz}$ complex, the binding is genuinely $\eta^6{:}\eta^6$, as shown by the Yb–C distance ranges, 2.799(2)–2.945(2) and 2.860(2)–3.050(2) Å despite an increase in the formal coordination number. The $\eta^6{:}\eta^6$ bonding of the BPh_4^- ligand is facilitated by the small 'bite' angle of the pyrazolate ligand; similar effects are noted in lanthanoid nitrate complexes [1]. Similar to the above complexes, the high Lewis acidity of the Yb centre was indicated by relatively short Yb–N bond distances to the pyrazolate ligand [17b]. The successful isolation of the pyrazolate complex contrasts the failure of the analogous reaction with $[\mathrm{Yb}(\mathrm{C}_6\mathrm{F}_5)(\mathrm{thf})_5][\mathrm{BPh}_4]$ and $\mathrm{Bu}^t{}_2\mathrm{pzH}$ and encourages exploration of both $[\mathrm{Yb}\{\mathrm{N}(\mathrm{SiMe}_3)_2\}(\mathrm{thf})\mathrm{BPh}_4]$ and $[\mathrm{Yb}\{\mathrm{N}(\mathrm{SiMe}_3)_2\}\mathrm{BPh}_4]$ as precursors of new reactive species.

4. Conclusions

The isolation of organolanthanoid(II) tetraphenylborates is problematic in donor solvents, largely due to the ease of formation of the solvated dicationic $[\mathrm{Ln}(\mathrm{S})_n][\mathrm{BPh}_4]_2$; the remarkable exception being $[\mathrm{Ln}(\mathrm{C}_6\mathrm{F}_5)(\mathrm{thf})_5][\mathrm{BPh}_4]$ (Ln = Eu, Yb). By contrast, restriction of the availability of neutral donors leads to a new family of unsymmetrical lanthanoid(II) complexes in which the BPh_4^- anion acts as a bulky, face-capping coordinating ligand. This has recently been extended by Evans and co-workers to include analogous $[\mathrm{LnCp^*BPh}_4]$ complexes with η^6-Ph–Ln interactions [30]. The observation of several forms of BPh_4^- binding in these $\mathrm{Yb}\{\mathrm{N}(\mathrm{SiMe}_3)_2\}\mathrm{BPh}_4$ complexes clearly shows the considerable coordinative flexibility of the BPh_4^- ligand. Furthermore, in $\mathrm{C}_6\mathrm{D}_6$ solution the bound and free Ph groups are indistinguishable by NMR suggesting a dynamic equalization process possibly involving solvent displacement of a bound Ph ring, opening the door for substrate coordination (and subsequent reaction chemistry) at the ytterbium(II) centre in these molecules.

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