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Linkage isomerism and C–H activation in an ytterbium(II) tetraphenylborate

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Reaction of $[Yb\{N(SiMe_3)_2\}_2(thf)_2]$ with $[Me_3NH][BPh_4]$ (1 : 1) in PhMe gives a mixture of products including $[Yb\{N(SiMe_3)_2\}(thf)BPh_4]$ (1), which exhibits two structural forms, and $[Yb\{N(SiMe_3)SiMe_2CH_2BPh_3\}(thf)_2]$ (2) with an unusual silylamidoborate ligand.

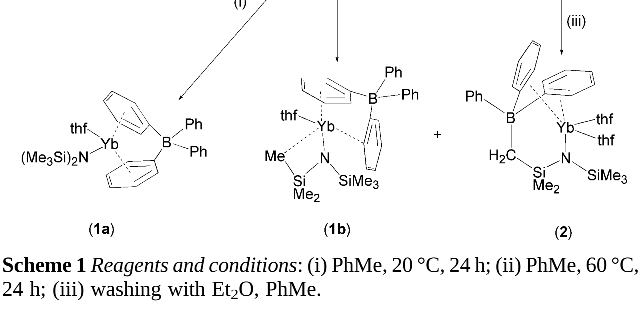
Cationic organolanthanoid(III) complexes $[Ln(L)_2]^+[A]^-$ (*e.g.* L = C_5Me_5) are rare but may show unusual reactivity due to enhanced Lewis acid character.[1] Of the currently known examples, the BPh_4 anion is often the counter ion[2–5] and is typically non-coordinating. The only exceptions occur in unsolvated complexes where the organoborate anions exhibit Ph–Ln contacts[3,4] (*e.g.* in $[Sm(C_5Me_5)_2(\eta^2\text{-}Ph)_2BPh_2]$[4]). Lanthanoid(II) tetraphenylborates are restricted to discrete solvated ionic complexes (*e.g.* $[\{Zr_2(O^iPr)_9\}Yb(thf)_2][BPh_4]$[5], and $[Ln(S)_x][BPh_4]_2$, S = solvent[6]) but unusual binding of the tetraphenylborate anion to a lanthanoid(II) cation may be possible by restricting the availability of competing donors. We now report the synthesis of an ytterbium(II) tetraphenylborate that exhibits π-Ph–Yb contacts, in *two linkage isomers*, and gives a surprising C–H activation product.

The reaction of $[Yb\{N(SiMe_3)_2\}_2(thf)_2]$[7] with one equivalent of $[Me_3NH][BPh_4]$ in PhMe at room temperature gave red–orange $[Yb\{N(SiMe_3)_2\}(thf)BPh_4]$ (**1a**) (Scheme 1, (i)) but in very low yield, crystallising from PhMe–hexane at −20 °C along with unreacted Yb reagent.† An attempt to drive reaction (i) to completion by heating gave a mixture of products as indicated by NMR spectroscopy. Crystallisation from hot PhMe yielded an adequate quantity of red **1b** (Scheme 1, (ii)).† The spectroscopic and analytical data were consistent with the composition of **1a** (above), but X-ray crystallography revealed a different structural form. From a separate preparation, a small number of red–orange crystals were isolated after a different workup (Scheme 1 (iii)).† These proved to be a highly novel product $[Yb\{N(SiMe_3)SiMe_2CH_2BPh_3\}(thf)_2]$ (**2**), possessing an unusual $N(SiMe_3)(SiMe_2CH_2BPh_3)^{2-}$ ligand.

Although **1a** was obtained only in a minor amount compared with **1b**, the Ln-BPh_4 binding is the more striking and is considered in more detail. The solid-state structure‡ of **1a** (Fig. 1) has a new (for Ln) pseudo-metallocene motif comprising a central ytterbium atom π-bound to two phenyl rings of the BPh_4 anion, one $N(SiMe_3)_2$ ligand and a thf. Lanthanoid-π-arene coordination is unusual[8] by comparison with transition metal chemistry where binding of BAr_4^- analogous to **1a** has been observed.[9] The coordination to ytterbium of the two phenyl rings (Fig. 1) is not identical with shorter distances to C(11)–C(16), defining an η^6-Ph(B)–Yb interaction, the first for a lanthanoid tetraphenylborate complex (*cf* η^6-Ph–Sc of a benzyl group in $[Sc(ArNC(Me)CHC(Me)NAr)(CH_2Ph)\text{-}B(CH_2Ph)(C_6F_5)_3]$ (Ar = C_6H_3-2,6-$Pr^i{}_2$)[10]). The Yb–C distance ranges are similar to those of intramolecular η^6-Ar–Yb^{II} interactions in $[Yb(SC_6H_3\text{-}2,6\text{-}Ar_2)_2]$ Ar = C_6H_2-2,4,6-$Pr^i{}_3$ (2.824(8)–3.139(8) Å),[11] and only marginally longer than for η^6-C_6Me_6-Eu^{II} in $[Eu(C_6Me_6)(AlCl_4)_2]_4$ (2.917(15)–3.066(12) Å)[12] after accounting for ionic radii differences. The generally longer distances to C(21)–C(26) and particularly to C(23) (3.243(3) Å) and C(24) (3.297(3) Å), suggest an η^4 attachment of the second Ph group. The C(11)–B–C(21) angle is substantially reduced (98.8(2)° *cf* 107.5(3)–115.5(3)° for the remaining C–B–C angles in **1a**) attributable to chelation of the BPh_4 anion to ytterbium. Thus **1a** bears a striking resemblance to the ubiquitous $LnCp_2X(S)$ (X = anionic ligand, S = solvent) though the cent–Yb–cent angle (110.5°) is much smaller in **1a** (*cf* ~125–130° for $LnCp_2$ species).

The major structural differences between the two forms **1a** and **1b** (see CCDC 192055) lie in the π-Ph coordination, with **1b** having a similar η^6-Ph interaction (Yb–C 2.802(4)–2.907(4) Å) but the second phenyl group is η^1 bound (Yb–C 2.763(4) Å). This change is accompanied by a widening of the N–Yb–O angle (114.9(1)° in **1b**) and the presence of an agostic Yb···Me contact in **1b** (Yb···C(1) 3.123(4) Å). The latter, characteristic of lanthanoid $N(SiMe_3)_2$ complexes (*e.g.* ref. 13), is absent in **1a** (closest separation Yb···C(6) 3.46 Å).

The above descriptions of **1a** and **1b** imply formal coordination numbers for Yb of 7 and 6 (or 7 with the agostic methyl) respectively, but the Yb–N distances (2.285(3) Å in **1b**) are *shorter* than those of 4-coordinate $[Yb\{N(SiMe_3)_2\}_2(dmpe)]$ (2.331(13) Å) (dmpe = 1,2-bis(dimethylphosphino)ethane)[14] and $[Yb\{N(SiMe_3)(C_6H_3\text{-}2,6\text{-}Pr^i{}_2)\}_2(thf)_2]$ 2.354(7) Å),[7] whilst the Yb–O bonds (2.352(3) in **1b**) are similar to those in 4-coordinate $[Yb(L)_2(thf)_2]$ (L = $N(SiMe_3)(C_6H_3\text{-}2,6\text{-}Pr^i{}_2)$



Scheme 1 *Reagents and conditions*: (i) PhMe, 20 °C, 24 h; (ii) PhMe, 60 °C, 24 h; (iii) washing with Et_2O, PhMe.

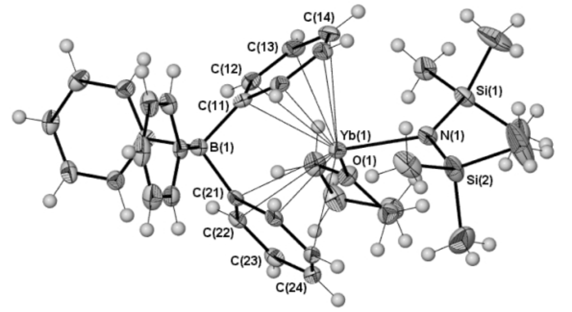


Fig. 1 Molecular structure of **1a**. Selected distances (Å) and angles (°): Yb–N(1) 2.314(2), Yb–O(1) 2.346(2), Yb–C(11–16) 2.855(3), 2.833(3), 2.919(3), 2.990(3), 2.978(3), 2.894(3), Yb–C(21–26) 2.946(3), 3.128(3), 3.243(3), 3.297(3), 3.030(3), 2.871(3), N(1)–Yb–O(1) 90.30(9).

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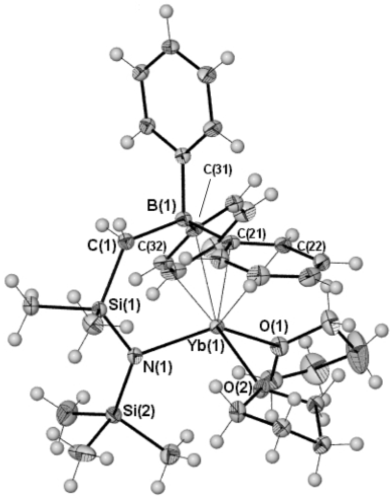

Fig. 2 Molecular structure of **2**. Selected distances (Å) and angles (°): Yb–N(1) 2.285(2), Yb–O(1) 2.378(2), Yb–O(2) 2.410(2), Yb–C(21) 2.635(3), Yb–C(22) 2.914(3), Yb–C(31) 2.792(3), Yb–C(32) 2.869(3), B(1)–C(1) 1.659(4), Si(1)–C(1) 1.896(3), B(1)–C(1)–Si(1) 132.8(2).

2.390(6) Å).[7] This suggests a strongly Lewis acidic centre potentially able to activate C–H bonds.

The solid-state structure‡ of **2** (Fig. 2) clearly shows the newly formed $SiMe_2$–CH_2–BPh_3 linkage with the Si–C(1) and B–C(1) bonds being typical and the $N(SiMe_3)SiMe_2CH_2BPh_3{}^{2-}$ ligand bound to ytterbium through the nitrogen and two η^2-Ph interactions from the BPh_3 group. Two thf ligands give overall 5 coordination. Binding of the silylamidoborate ligand to ytterbium is accompanied by a marked widening of the B(1)–C(1)–Si(1) angle from tetrahedral. The Yb–N bond is shorter than in **1a** (but identical to that of **1b**) whereas the Yb–O distances are longer but both are shorter than those of 6-coordinate $[Yb(C_5Me_5)\{N(SiMe_3)_2\}(thf)_2]$ (Yb–N 2.347(3), Yb–O 2.424(3), 2.469(3) Å).[15] The Yb–C distances are comparable to those of a Yb^{II}-π-olefin complex (*e.g.* $[Yb(C_5Me_5)_2(\mu\text{-}CH_2=CH_2)PtMe_2$ 2.781(±0.006) Å[16]). However, the binding of C(21) and C(22) is unsymmetrical, with a short Yb(1)–C(21) bond close to the average (2.60 Å) for a bridging *phenyl anion* in $[YbPh_2(thf)(\mu\text{-}Ph)_3Yb(thf)_3]$ (range 2.48(3)–2.75(4) Å).[17]

In 5f-element chemistry, reaction of $[U\{N(SiMe_3)_2\}_3H]$ with $B(C_6F_5)_3$[18] enables the hydride generated $NSiMe_2CH_2{}^-$ group to be captured by the strong Lewis acid giving $[U\{N(SiMe_3)_2\}_2\{N(SiMe_3)(SiMe_2CH_2B(C_6F_5)_3)\}]$ with a silylamidoborate ligand similar to that of **2**. Thermally induced nucleophilic substitution at a saturated boron by $PhCC^-$ has recently been observed for $[Sm\{HB(Me_2pz)_3\}_2(L)]$ eliminating the good leaving group Me_2pz^- and forming a $Sm\{HB(Me_2pz)_2(CCPh)\}$ moiety.[19] By contrast, the formation of **2** occurs readily despite the lack of a strong base functionality to induce Si–C–H deprotonation (*cf* deprotonation–cyclization of $[Ln\{N(SiMe_3)_2\}_3]$ by $NaN(SiMe_3)_2$[20]), a Lewis acidic boron to capture the incipient carbanion, or even a facile leaving group on boron. Accordingly, Yb-induced C–H and perhaps C–B activation is indicated, the latter also possibly consequent on π-Ph(B)···Yb bonding in **1**.

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Notes and references

† *Syntheses*: **1a**: $[Yb\{N(SiMe_3)_2\}_2(thf)_2]$ (0.68 g 1.0 mmol) and $[Me_3NH][BPh_4]$ (0.38 g 1.0 mmol) in PhMe (30 mL) was stirred at room temperature for 24 h and gave a mixture of orange needles of $[Yb\{N(SiMe_3)_2\}_2(thf)_2]$ and a few red–orange prisms of **1a** (identified by X-ray crystallography) after filtration, addition of hexane, and cooling to −20 °C. **1b**: $[Yb\{N(SiMe_3)_2\}_2(thf)_2]$ (1.36 g 2.0 mmol) and $[Me_3NH][BPh_4]$ (0.76 g 2.0 mmol) in PhMe (40 mL) was stirred at 60 °C for 24 h then filtered hot. The concentrated filtrate gave red–orange **1b** on standing (26%). Anal. Found for $C_{34}H_{46}BNOSi_2Yb$: C 56.6, H 6.2, N 1.8. Calc. C 56.4, H 6.4, N 1.9%. IR(Nujol)/cm^{-1}: 1581w, 1565w, 1312w, 1251m, 1240m, 1151m, 1066w, 1005vs, 869m, 825m, 779m, 737s, 711s, 659w. ^{1}H NMR (C_6D_6 200 MHz)/ppm: 7.80 (br s, 8H, *o*-H), 7.18 (br s, 8H, *m*-H), 6.95 (br s, 4H, *p*-H), 3.30 (vbr s, 4H, thf), 1.30 (vbr s, 4H, thf), −0.03 (s, 18H, $SiMe_3$). **2**: $[Yb\{N(SiMe_3)_2\}_2(thf)_2]$ (0.68 g 1.0 mmol) and $[Me_3NH][BPh_4]$ (0.38 g 1.0 mmol) in PhMe (30 mL) was stirred at 60 °C for 24 h. The filtered and concentrated solution gave a mixture of pale yellow and red–orange crystals. Washing with diethyl ether and recrystallisation of the residue from PhMe gave solely red–orange **2** (8% yield). IR(Nujol)/cm^{-1}: 1583w, 1312w, 1238m, 1129w, 1086w, 1031s, 917w, 865m, 831s, 792m, 753m, 742m, 717m, 706m, 656w. ^{1}H NMR (C_6D_6 400 MHz)/ppm: 7.88 (d, ^3J 6.7 Hz, 6H, *o*-H), 7.18 (t, ^3J 7.5Hz, 6H, *m*-H), 6.99 (t, ^3J 7.3 Hz, 3H, *p*-H), 3.04 (br s, 8H, thf), 1.14 (br s, 8H, thf), 1.03 (br s, 2H, CH_2), 0.69 (s, 6H, $SiMe_2$), 0.23 (s, 9H, $SiMe_3$).

‡ *Crystal data*: **1a**: $C_{34}H_{46}BNOSi_2Yb$ (724.75) monoclinic ($P2_1/c$) a 9.6210(1), b 15.7886(2), c 22.2434(2) Å, β 92.931(1)°, V 3374(1) Å^3, $\rho_{calc}(Z = 4)$ 1.427 g cm^{-3}, $\mu(MoK_\alpha)$ 2.90 mm^{-1}; 8258 unique (R_{int} 0.065) reflections converged to R = 0.068, wR_2 = 0.065 (all data). **1b**: $C_{34}H_{46}BNOSi_2Yb$ (724.75) orthorhombic ($Pca2_1$) a 14.1600(2), b 14.5302(2), c 16.3056(2) Å, V 3354(1) Å^3, $\rho_{calc}(Z = 4)$ 1.435 g cm^{-3}, $\mu(MoK_\alpha)$ 2.89 mm^{-1}; 7833 unique (R_{int} 0.069) reflections converged to R = 0.055, wR_2 = 0.065 (all data); x_{abs} 0.02(1). **2**: $C_{32}H_{48}BNO_2Si_2Yb$ (718.74) monoclinic ($P2_1/n$) a 9.9426(1), b 18.7251(2), c 18.3353(2) Å, β 101.633(1)°, V 3343(1) Å^3, $\rho_{calc}(Z = 4)$ 1.428 g cm^{-3}, $\mu(MoK_\alpha)$ 2.90 mm^{-1}; 8208 unique (R_{int} 0.079) reflections converged to R = 0.039, wR_2 = 0.091 (all data). (Enraf-Nonius CCD, λ(Mo-Kα) = 0.71073 Å, 123 K). CCDC reference numbers 192054–192056. See http://www.rsc.org/suppdata/cc/b2/b208149k/ for crystallographic data in CIF or other electronic format.

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