Yttrium metallocene borane chemistry: isolation of 9-BBN substitution and coordination complexes in a single crystal, $\{(C_5Me_5)_2Y[\eta^3\text{-}C_3H_4(BC_8H_{14})]\}$ and $\{(C_5Me_5)_2Y(\mu\text{-}H)_2BC_8H_{14}\}$

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$(C_5Me_5)_2Y(\eta^3\text{-}C_3H_5)$ reacts with 9-borabicyclo[3.3.1]nonane, 9-BBN, to form single crystals containing *both* a borane-substituted allyl complex, $(C_5Me_5)_2Y[\eta^3\text{-}C_3H_4(BC_8H_{14})]$, and a borohydride, $(C_5Me_5)_2Y(\mu\text{-}H)_2BC_8H_{14}$, that can be synthesized directly from 9-BBN and the yttrium hydride, $[(C_5Me_5)_2YH]_x$.

Although the organoaluminium chemistry of yttrium and lanthanide metallocenes has proven to be a fertile source of unusual structure and reactivity for both aluminium and the lanthanide-like metals,[1,2] relatively little effort has been directed to the congeneric alkylborane chemistry of yttrium and the lanthanides. To expand upon the few reports in the literature in this area,[3] we examined the reaction of the common borane reagent, 9-BBN, HBC_8H_{14}, with the yttrium allyl complex, $(C_5Me_5)_2Y(\eta^3\text{-}C_3H_5)$, **1**, as a representative example of a metallocene that provides facile access to M–C bond reactivity in common solvents.[4] We report here that single crystals obtained from this reaction contain two unexpected yttrium metallocene borane complexes.

Complex **1** reacts with 9-BBN in toluene over a 24 h period to form a yellow powder, **2**, that displays three resonances in a 2 : 1 : 1 ratio in the $(C_5Me_5)^-$ region of the ^1H NMR spectrum.† X-Ray crystallographic analysis of single crystals of **2** revealed that it is comprised of *two* yttrium metallocene borane complexes, namely $(C_5Me_5)_2Y[\eta^3\text{-}C_3H_4(BC_8H_{14})]$, **3**, and $(C_5Me_5)_2Y(\mu\text{-}H)_2BC_8H_{14}$, **4** (Fig. 1)‡ and eqn (1).

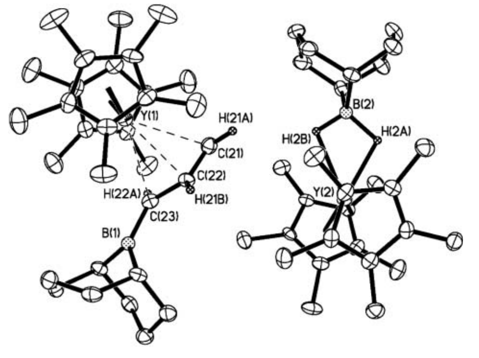
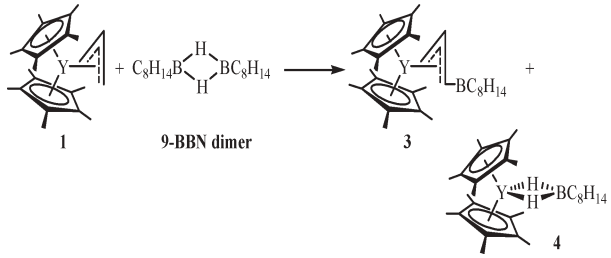
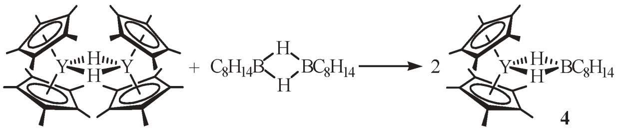


Fig. 1 Thermal ellipsoid plot drawn at the 50% probability level of **2**, containing the yttrium metallocene borane complexes, $(C_5Me_5)_2Y[\eta^3\text{-}C_3H_4(BC_8H_{14})]$, **3**, and $(C_5Me_5)_2Y(\mu\text{-}H)_2(BC_8H_{14})$, **4**, in a single crystal.



(1)

Since **4** is the formal result of adding 9-BBN to $[(C_5Me_5)_2YH]_x$, an independent synthesis according to eqn (2) was attempted. Indeed, complex **4** was obtained *via* eqn (2) and independently characterized by X-ray crystallography.§ However, the X-ray data on **4** alone were of limited quality and revealed only the atom connectivity. This structure was identical to the well defined data on **4** in single crystals of **2**. The ^1H NMR spectrum obtained from the isolated single crystals of **4** displayed resonances that matched a subset of those in the ^1H NMR spectrum of **2** as expected. The remaining resonances from the ^1H NMR spectrum of **2** were consistent with **3**.



(2)

The structural parameters of **3** (Fig. 2), are compared in Table 1 to those of $(C_5Me_5)_2Y(\eta^3\text{-}C_3H_5)$,[4] **1** and $(C_5Me_5)_2Sm(\eta^3\text{-}C_3H_4Ph)(OC_8H_8)$,[5] **5**, the closest example of a lanthanide metallocene allyl functionalized with a large group on the terminal

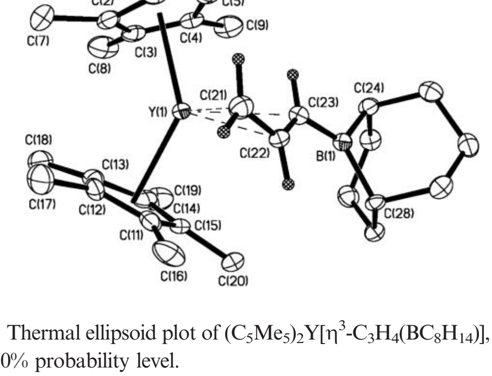


Fig. 2 Thermal ellipsoid plot of $(C_5Me_5)_2Y[\eta^3\text{-}C_3H_4(BC_8H_{14})]$, **3**, drawn at the 50% probability level.

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Table 1 Selected bond distances (Å) and angles (°) for $(C_5Me_5)_2Y[\eta^3\text{-}C_3H_4(BC_8H_{14})]$, **3**, $(C_5Me_5)_2Y(\eta^3\text{-}C_3H_5)$,[4] **1**, $(C_5Me_5)_2Sm[\eta^3\text{-}C_3H_4(C_6H_5)](OC_8H_8)$,[6] **5**, and $(C_5Me_5)_2Y[(\mu\text{-}H)_2BC_8H_{14}]$, **4**

	3	1	5	4
Ln	Y	Y	Sm	Y
Ln(1)–C(21)	2.681(5)	2.582(2)	2.643(3)	
Ln(1)–C(22)	2.661(5)	2.601(2)	2.769(2)	
Ln(1)–C(23)	2.632(5)	2.582(2)	2.922(3)	
Ln(1)–Cnt1	2.380	2.381	2.484	2.334
Ln(1)–Cnt2	2.360	2.362	2.507	2.354
C(21)–C(22)	1.364(7)	1.392(3)	1.396(4)	
C(22)–C(23)	1.430(7)	1.391(3)	1.359(4)	
Cnt1–Ln(1)–Cnt2	136.2	138.8	134.6	137.1
C(21)–C(22)–C(23)	126.0(5)	125.9(2)	126.3(3)	
C(21)–Ln(1)–C(22)	29.58(15)	31.14(7)	29.8(1)	
C(22)–Ln(1)–C(23)	31.34(15)	31.12(7)	27.5(1)	

carbon. The Y–(C_5Me_5 ring centroid) distances of **3** are almost identical to those of **1**. The Y(1)–C(21), Y(1)–C(22) and Y(1)–C(23) Y–C(allyl) distances in **3** are 2.681(5), 2.661(5) and 2.632(5) Å, respectively. These distances are slightly longer than the corresponding distances in **1**, 2.582(2), 2.601(2) and 2.582(2) Å, respectively, and are more disparate as is typical for substituted allyl complexes. For example, **5** has a much wider range of Sm–C(allyl) bond distances, 2.643(3), 2.769(2) and 2.922(3) Å. In **5** however, the longest Sm–C(allyl) bond involves the substituted carbon whereas the shortest Y–C(allyl) distance in **3** is found for the substituted carbon, C(23).

The molecular structure of **4** (Fig. 3) can be compared to the *divalent* ytterbium and europium 9-BBN complexes, $(THF)_4Yb[(\mu\text{-}H)_2BC_8H_{14}]_2$,[3a] **6**, and $(THF)_4Eu[(\mu\text{-}H)_2BC_8H_{14}]_2$,[3a] **7**, and the *trivalent* yttrium tetrahydroborate, $(MeOCH_2CH_2C_5H_4)_2Y[(\mu\text{-}H)_2BH_2]$,[6] **8**. The metrical parameters of **4** associated with the $[(C_5Me_5)_2Y]^{1+}$ fragment are within the expected range (Table 1).[7] The bidentate bridging mode of the $[(\mu\text{-}H)_2BC_8H_{14}]^-$ ligand is common for hydroborates when coordinated to metals that are of comparable size to yttrium.[3a,8] The 2.767(6) Å Y···B distance in **4** is similar to the 2.876(7) Å Yb···B distance in **6** and the 2.920(7) Å Eu···B distance in **7**, when the 0.121 and 0.231 Å larger ionic radii of Yb^{2+} and Eu^{2+}, respectively, are taken into account.[9] The Y···B distance is also similar to that in **8**, 2.817 Å.

One possible route to the formation of complexes **3** and **4** is shown in Scheme 1. Although there is precedence for each step in the proposed reaction sequence, the combination of these steps has not been observed previously. The first step involves a conventional addition of 9-BBN to an olefin.[10] This is unusual in that the olefin arises from the allyl metallocene starting material with the allyl group in an η^1-coordination mode, *i.e.* $(C_5Me_5)_2Y(\eta^1\text{-}CH_2CH{=}CH_2)$, **A**. Typically, η^1-allyl reactivity in yttrium and lanthanide metallocenes arises from the Ln–C single bond, not the olefin. The bulky alkyl moiety that results, "$(C_5Me_5)_2Y(CH_2CH_2CH_2BC_8H_{14})$," **B**, could β-hydrogen eliminate to form the known $[(C_5Me_5)_2YH]_x$[11] and the 9-BBN-substituted olefin, $CH_2{=}CHCH_2(BC_8H_{14})$. Trapping of the $[(C_5Me_5)_2YH]_x$ formed in this step with 9-BBN according to eqn (2) would generate component **4** of the product mixture. In order to obtain **3**, $CH_2{=}CHCH_2(BC_8H_{14})$ could be metalated by unreacted **A** present in solution, resulting in the liberation of propene. Alternatively, complex **B** or $[(C_5Me_5)_2YH]_x$ also have the potential to metalate $CH_2{=}CHCH_2(BC_8H_{14})$ to form **3** and $CH_3CH_2CH_2(BC_8H_{14})$ or H_2, respectively. The reaction of one equivalent of **1** with 9-BBN dimer (Y : B ratio of 1 : 2) gives predominantly **4**, which suggests that the yttrium hydride is trapped faster by 9-BBN, eqn (4), than it is metalated, eqn (5). When four equivalents of **1** react with 9-BBN dimer (Y : B ratio 2 : 1), the ^{1}H NMR spectrum is consistent with the generation of an equimolar mixture of **3** and **4** with excess **1** also present. This again suggests that the reaction is eqn (4) proceeds at a rate faster than that of eqn (5).

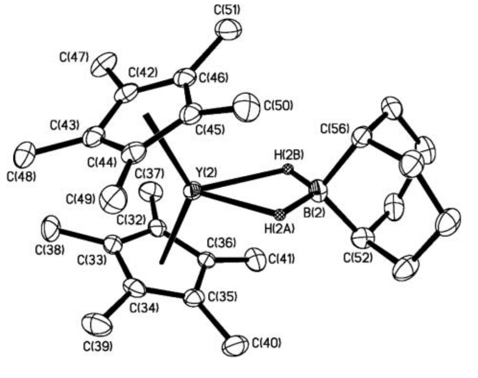
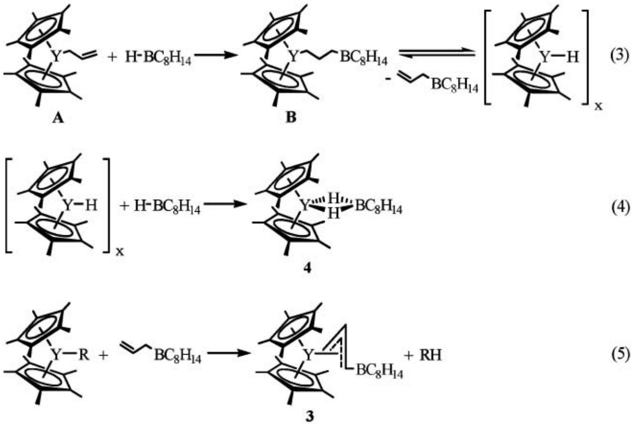


Fig. 3 Thermal ellipsoid plot of $(C_5Me_5)_2Y(\mu\text{-}H)_2(BC_8H_{14})$, **4**, drawn at the 50% probability level.



(R = H, C_3H_5, $C_3H_6BC_8H_{14}$)

Scheme 1

Attempts to identify the by-products in eqn (1) were made by conducting the reaction in a sealed J. Young NMR tube. ^{1}H NMR spectroscopy revealed resonances arising from **3** and **4**, but neither H_2 nor propene were observed by NMR or GC-MS analysis of the gases in the NMR tube. Hence, **B** is the most likely metalating agent. ^{11}B NMR spectroscopy is consistent with this. The ^{11}B NMR spectrum revealed at least three boron-containing species in the reaction mixture. Complex **4** was unambiguously identified by comparing the spectrum of the bulk reaction mixture with the 3.45 ppm resonance of **4** generated from $[(C_5Me_5)_2YH]_x$ and 9-BBN. The two other major resonances present in the ^{11}B NMR spectrum display chemical shifts at 87.61 and 66.50 ppm, respectively. The resonance at 87.61 ppm falls within the narrow range of 80–90 ppm for a trisubstituted alkylborane species, BR_3,[12] and could arise from the alkyl-substituted borane, $CH_3CH_2CH_2BC_8H_{14}$, in Scheme 1. The 66.50 ppm resonance is more consistent with the 50–70 ppm range reported for olefin-substituted borane species such as (RCH=CH)BR_2 and could arise from **3**.[12] However, since these are general trends, they do not provide definitive evidence of the mechanism for the formation of **2**, as other reaction pathways are also possible.

In summary, $(C_5Me_5)_2Y(\eta^3\text{-}C_3H_5)$ reacted with 9-BBN as an olefin complex rather than an alkyl metallocene. This suggests that 9-BBN could be useful to derivatize other lanthanide metallocene complexes that contain ligands with variable coordination modes where unsaturated components could be involved. 9-BBN also proved to be effective in trapping a metallocene hydride intermediate. Surprisingly, the single crystal of **2**, containing two different yttrium metallocene borane complexes, **3** and **4**, gave better structural data than the crystal of **4** alone. Clearly, new avenues of f element chemistry can be pursued *via* organoboranes.

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Notes and references

† *Synthesis* of **2**: In an argon-filled glovebox free of coordinating solvents, a yellow solution of $(C_5Me_5)_2Y(\eta^3\text{-}C_3H_5)^4$ (68 mg, 0.17 mmol) in 10 mL of toluene was added to 9-BBN dimer (21 mg, 0.085 mmol). After the mixture was stirred for 24 h, the pale yellow solution was evaporated to dryness to yield a bright yellow tacky solid. The yellow solid was washed with hexanes and evaporated to dryness to yield a yellow powder (81 mg, 95%). Pale yellow crystals suitable for X-ray diffraction were grown by slow evaporation of benzene-d_6 at 25 °C. ^{1}H NMR (500 MHz, benzene-d_6) δ 7.72 (m, 1H, $\{C_3H_4(BC_8H_{14})\}$), 4.90 (dd, J = 16, 3 Hz, 1H, $\{C_3H_4(BC_8H_{14})\}$), 4.06 (dt, J = 16 Hz, 1H, $\{C_3H_4(BC_8H_{14})\}$), 2.89 (dd, J = 9, 1.5 Hz, 1H, $\{C_3H_4(BC_8H_{14})\}$), 0.87–2.42 (m, $\{(\mu\text{-}H)_2BC_8H_{14})\}$ and $\{C_3H_4(BC_8H_{14})\}$), 1.94 (s, 15H, C_5Me_5), 1.88 (s, 15H, C_5Me_5), 1.87 (s, 30H, C_5Me_5). $^{11}B\{^1H\}$ NMR (160 MHz, benzene-d_6) δ 87.61, 66.50, 3.45. IR (thin film, cm^{-1}) 2910w, 2868w, 2729m, 2281m, 1911s, 1567m, 1444w, 1413w, 1382w, 1336m, 1316m, 1293m, 1262m, 1224m, 1204m, 1173m, 1150m, 1081w, 1061w, 1019w, 946m, 892m, 865m, 803s, 672s. Anal. Calc. for $C_{59}H_{94}B_2Y_2$: C, 70.66; H, 9.45; B, 2.16; Y, 17.73. Found: C, 71.06; H, 9.65; B, 2.09; Y, 17.40%.

‡ *Crystallographic data* for **2**: $C_{59}H_{94}B_2Y_2$, M = 1002.78, triclinic, space group $P\bar{1}$, a = 9.5275(19), b = 14.801(3), c = 19.630(4) Å, α = 89.906(4), β = 77.076(4), γ = 88.648(4)°, V = 2697.2(9) Å^3, T = 163(2) K, Z = 2, μ(Mo-Kα) = 2.176 mm^{-1}, 26 140 reflections measured on a Bruker CCD diffractometer, 10 964 unique (R_{int} = 0.0498) which were used in all calculations. The final $R1$ was 0.0610 ($I > 2.0\sigma(I)$) and $wR2$ (all data, 0.80 Å) was 0.1560. The SMART program package[13] was used to determine the unit-cell parameters and for data collection (30 s frame^{-1} scan time for a sphere of diffraction data). The raw frame data was processed using SAINT[14] and SADABS[15] to yield the reflection data file. Subsequent calculations were carried out using the SHELXTL program.[16] The structure was solved by direct methods and refined on F^2 by full-matrix least-squares techniques. CCDC 652170. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b709841c

§ *Independent synthesis* of **4**: In an argon-filled glovebox free of coordinating solvents, a pale orange solution of $[(C_5Me_5)_2YH]_x$ (48 mg, 0.07 mmol) in 10 mL of methylcyclohexane was added to 9-BBN dimer (21 mg, 0.09 mmol). After the mixture was stirred overnight, the pale yellow solution was evaporated to dryness to yield **4** as a white solid (63 mg, 97%). Colorless crystals suitable for X-ray diffraction were grown by slow evaporation of benzene-d_6 at 25 °C. ^{1}H NMR (500 MHz, benzene-d_6) δ 2.42–1.51 (m, α- β- and γ-H of $\{BC_8H_{14})\}$), 1.87 (s, 30H, C_5Me_5), 0.87 (d, J = 7 Hz, 2H, μ-H of $\{(\mu\text{-}H)_2BC_8H_{14})\}$). $^{11}B\{^1H\}$ NMR (160 MHz, benzene-d_6) δ 3.45. IR (thin film, cm^{-1}) 2914w, 2887w, 2860w, 2841w, 1563s, 1471m, 1147m, 1417m, 1390m, 1343m, 1320m, 1289m, 1262m, 1208s, 1162s, 1061s, 1081w, 1031w, 977m, 919s, 884m, 803s, 679w.

Crystallographic data for **4**: $C_{28}H_{46}BY$, M = 482.37, triclinic, space group $P\bar{1}$, a = 9.372(19), b = 15.06(3), c = 20.23(4) Å, α = 69.47(3), β = 77.66(3), γ = 87.88(4)°, V = 2609(9) Å^3.

1 A. Fischbach and R. Anwander, *Adv. Polym. Sci.*, 2006, **204**, 155, and references therein.

2 (*a*) J. Holton, M. F. Lappert, D. G. H. Ballard, R. Pearce, J. L. Atwood and W. E. Hunter, *J. Chem. Soc., Dalton Trans.*, 1979, 45; (*b*) J. M. Boncella and R. A. Andersen, *Organometallics*, 1985, **4**, 205; (*c*) P. L. Watson and G. W. Parshall, *Acc. Chem. Res.*, 1985, **18**, 51; (*d*) W. J. Evans, L. R. Chamberlain, T. A. Ulibarri and J. W. Ziller, *J. Am. Chem. Soc.*, 1988, **110**, 6423; (*e*) W. T. Klooster, R. S. Lu, R. Anwander, W. J. Evans, T. F. Koetzle and R. Bau, *Angew. Chem., Int. Ed.*, 1998, **37**, 1268; (*f*) H. Nakamura, Y. Nakayama, H. Yasuda, T. Maruo, N. Kanehisa and Y. Kai, *Organometallics*, 2000, **19**, 5392; (*g*) R. Anwander, M. G. Klimpel, H. M. Dietrich, D. J. Shorokhov and W. Scherer, *Chem. Commun.*, 2003, 1008; (*h*) T. J. Woodman, Y. Sarazin, G. Fink, K. Hauschild and M. Bochmann, *Macromolecules*, 2005, **38**, 3060; (*i*) W. J. Evans, T. M. Champagne and J. W. Ziller, *Organometallics*, 2005, **24**, 4882; (*j*) W. J. Evans, T. M. Champagne and J. W. Ziller, *Chem. Commun.*, 2005, 5925; (*k*) H. M. Dietrich, O. Schuster, K. W. Törnoos and R. W. Anwander, *Angew. Chem., Int. Ed.*, 2006, 4858.

3 (*a*) X. Chen, S. Lim, C. E. Plečnik, S. Liu, B. Du, E. A. Meyers and S. G. Shore, *Inorg. Chem.*, 2004, **43**, 692; (*b*) J. L. Galler, S. Goodchild, J. Gould, R. McDonald and A. Sella, *Polyhedron*, 2004, **23**, 253; (*c*) X. Chen, S. Lim, C. E. Plečnik, S. Liu, B. Du, E. A. Meyers and S. G. Shore, *Inorg. Chem.*, 2005, **44**, 6052; (*d*) W. J. Evans, J. M. Perotti and J. W. Ziller, *Inorg. Chem.*, 2005, **44**, 5820; (*e*) H. Shen, H.-S. Chan and Z. Xie, *Organometallics*, 2006, **25**, 2617.

4 W. J. Evans, S. A. Kozimor, J. C. Brady, B. L. Davis, G. W. Nyce, C. A. Seibel, J. W. Ziller and R. J. Doedens, *Organometallics*, 2005, **24**, 2269.

5 W. J. Evans, T. A. Ulibarri and J. W. Ziller, *J. Am. Chem. Soc.*, 1990, **112**, 2314.

6 D. A. Laske, R. Duchateau and J. H. Teuben, *J. Organomet. Chem.*, 1993, **462**, 149.

7 W. J. Evans and S. E. Foster, *J. Organomet. Chem.*, 1992, **433**, 79.

8 M. F. Lappert, A. Singh, J. L. Atwood and W. E. Hunter, *J. Chem. Soc., Chem. Commun.*, 1983, 206.

9 R. D. Shannon, *Acta Crystallogr., Sect. A*, 1976, **32**, 751.

10 A. Pelter, K. Smith and H. C. Brown, *Borane Reagents*, Academic Press, New York, 1988.

11 K. H. DenHaan, Y. Wielstra and J. H. Teuben, *Organometallics*, 1987, **6**, 2053.

12 B. Wrackmeyer, *Annu. Rep. NMR Spectrosc.*, 1998, **20**, 61.

13 SMART Software Users Guide, Version 5.1, Bruker Analytical X-Ray Systems, Inc., Madison, WI, 1999.

14 SAINT Software Users Guide, Version 6.0, Bruker Analytical X-Ray Systems, Inc., Madison, WI, 1999.

15 G. M. Sheldrick, SADABS, Version 2.10, Bruker Analytical X-Ray Systems, Inc., Madison, WI, 2002.

16 G. M. Sheldrick, SHELXTL Version 6.12, Bruker Analytical X-Ray Systems, Inc., Madison, WI, 2001.