Mechanochemical C−H bond activation: Synthesis of the tuckover hydrides, $(C_5Me_5)_2Ln(\mu\text{-}H)(\mu\text{-}\eta^1:\eta^5\text{-}CH_2C_5Me_4)Ln(C_5Me_5)$ from solvent-free reactions of $(C_5Me_5)_2Ln(\mu\text{-}Ph)_2BPh_2$ with KC_5Me_5

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ABSTRACT

Attempts to synthesize the sterically crowded complexes $(C_5Me_5)_3Ln$ of the smallest lanthanide metals, $Ln = Tm$ and Lu, from $(C_5Me_5)_2Ln(\mu\text{-}Ph)_2BPh_2$ and KC_5Me_5 via mechanochemical methods has revealed C−H bond activation chemistry: the tuckover hydride complexes, $(C_5Me_5)_2Ln(\mu\text{-}H)(\mu\text{-}\eta^1:\eta^5\text{-}CH_2C_5Me_4)Ln(C_5Me_5)$, were observed in low crystalline yields. In the case of $Ln = Yb$, attempts to synthesize the cationic precursor, $(C_5Me_5)_2Yb(\mu\text{-}Ph)_2BPh_2$, from the reaction of $(C_5Me_5)_2Yb(\eta^3\text{-}C_3H_5)$ and $[HNEt_3][BPh_4]$ led to the reduction of the metal and the formation of the Yb(II) cationic complex, $(C_5Me_5)Yb(\mu\text{-}Ph)_2BPh_2$.
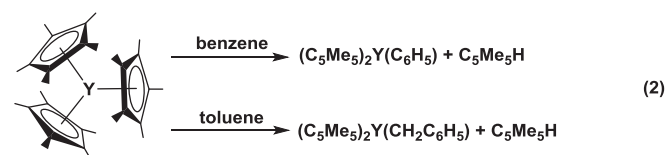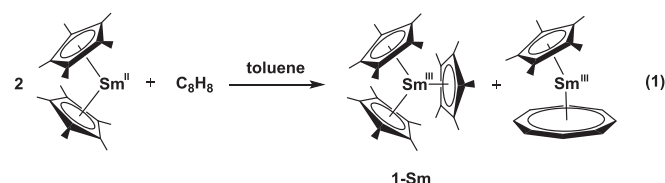© 2019 Elsevier B.V. All rights reserved.

1. Introduction

For several decades after the $(C_5Me_5)^{1-}$ ligand was introduced into organometallic chemistry [1−3], it was assumed that three of these large ligands could not be put around a single metal center since the cone angle of $(C_5Me_5)^{1-}$ was estimated to be 142° [4,5]. However, this assumption was overturned by the discovery of $(C_5Me_5)_3Sm$, **1-Sm**, which formed from the reaction of the Sm(II) complex, $(C_5Me_5)_2Sm$, with C_8H_8, eq 1 [6]. X-ray crystallographic analysis of **1-Sm** revealed that the cone angle in this complex was 120°. This "reduced" cone angle was achieved because the ligands were positioned further away from the metal than in traditional $(C_5Me_5)^{1-}$ complexes of samarium: the average Sm−C(ring) distance was ca. 0.1 Å longer than those of all other Sm(III) complexes previously characterized by X-ray crystallography [7]. Subsequently, $(C_5Me_5)_3M$ complexes were discovered with M = La [8], Ce [9], Pr [9], Nd [10], Gd [11], Y [11], U [12,13], and Th [14], all of which also had long M−C(C_5Me_5) distances compared to previously reported rare-earth cyclopentadienyl complexes [7].

Increased reactivity of the $(C_5Me_5)^{1-}$ ligand was observed due to the increased distance from the metal center. For example, with the exception of the thorium complex, $(C_5Me_5)_3M$ complexes were capable of ring opening THF [9,15] to make complexes with $[O(CH_2)_4(C_5Me_5)]^{1-}$ ligands. They also displayed chemistry consistent with "$(C_5Me_5)_2M(\eta^1\text{-}C_5Me_5)$" intermediates in ethylene polymerization, as well as one-electron reductive chemistry based on a $(C_5Me_5)^{1-}/(C_5Me_5)$ redox couple in reactions termed sterically-induced reduction [16]. In the case of yttrium, C−H bond activation was observed with aromatic solvents, benzene and toluene, to form phenyl and benzyl products, $(C_5Me_5)_2Y(C_6H_5)$ and $(C_5Me_5)_2Y(CH_2C_6H_5)$, respectively, eq 2 [11].

$$2 \ Sm^{II} + C_8H_8 \xrightarrow{\text{toluene}} Sm^{III} + Sm^{III} \quad (1)$$

1-Sm

$$Y \xrightarrow{\text{benzene}} (C_5Me_5)_2Y(C_6H_5) + C_5Me_5H$$

$$\xrightarrow{\text{toluene}} (C_5Me_5)_2Y(CH_2C_6H_5) + C_5Me_5H \quad (2)$$

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Most of the $(C_5Me_5)_3M$ complexes (M = La, Ce, Pr, Nd, Gd, U, Th) can be prepared from the reaction of the cationic complexes, $(C_5Me_5)_2M(\mu\text{-Ph})_2BPh_2$, with one equiv of KC_5Me_5 in benzene or toluene. Since $(C_5Me_5)_3Y$, **1-Y**, readily reacts with benzene and toluene, **1-Y** was prepared by reacting the bridged hydride complex, $[(C_5Me_5)_2YH]_2$, with 1,2,3,4-tetramethylfulvene (TMF) in methylcyclohexane (MCH), eq 3 [11].

$$\frac{1}{2}\ [(C_5Me_5)_2YH]_2\ +\quad\xrightarrow{\text{MCH}}\qquad\qquad\qquad (3)$$
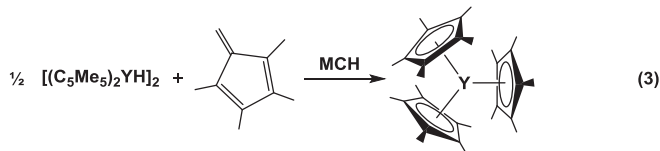
Recently, the sterically crowded $(C_5Me_5)_3Ln$, **1-Ln**, complexes of the smaller rare-earth metals, Ln = Tb, Dy, Ho, Er, and Y were successfully synthesized using mechanochemistry, eq 4 [17].

$$\cdots\ +\ KC_5Me_5\ \xrightarrow[-\ KBPh_4]{}\ \cdots \qquad (4)$$

Ln = Tb, Dy, Ho, Er, and Y   **1-Ln**
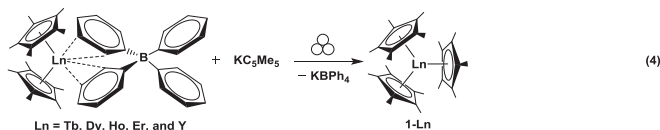
Specifically, the cationic metal precursors, $(C_5Me_5)_2Ln(\mu\text{-Ph})_2BPh_2$, were reacted in the solid state with KC_5Me_5 by ballmilling with stainless steel spheres of 6 mm diameter in a disperser tube. This synthetic approach was advantageous since it avoided the benzene and toluene solvents previously shown to react with **1-Y**, eq 2.

We report here the use of this solvent-free mechanochemical method with the smallest metals in the lanthanide series, which led to the identification of mechanochemical C−H bond activation pathways. Analogs of the known tuckover hydride complexes $(C_5Me_5)_2Ln(\mu\text{-H})(\mu\text{-}\eta^1{:}\eta^5\text{-}CH_2C_5Me_4)Ln(C_5Me_5)$ (Ln = Y [18], La [19], Sm [20], Lu [21]) arising from C−H bond activation of $(C_5Me_5)^{1-}$ ligands are isolated with Tm and Lu. For Yb, we find that attempts to make the $(C_5Me_5)_2Ln(\mu\text{-Ph})_2BPh_2$ precursor for this reaction leads to reduction and formation of the known Yb(II) cationic complex, $(C_5Me_5)Yb(\mu\text{-Ph})_2BPh_2$ [22].

2. Results and discussion

The cationic metal precursors, $(C_5Me_5)_2Ln(\mu\text{-Ph})_2BPh_2$, **2-Ln** (Ln = Tm, Lu), were successfully prepared following the established procedure for analogs of the other rare-earth metals, by reaction of $LnCl_3$ with 2 equiv KC_5Me_5 to make $(C_5Me_5)_2Ln(\mu\text{-Cl}_2)$ $K(THF)_x$, followed by conversion of the ate salt to $(C_5Me_5)_2Ln(\eta^3\text{-}C_3H_5)$, and protonolysis of the subsequent allyl complex with $[HNEt_3][BPh_4]$ [10,11]. Milling powders of pale orange **2-Tm** and colorless **2-Lu** with KC_5Me_5 using 6 mm diameter stainless steel balls in a BMT-20-S tube powered by an Ultra-Turrax Tube Drive gave a dark orange material with each metal. Extraction of the reaction product with pentane (Ln = Tm) or hexane (Ln = Lu) gave low yields of single crystals identified by X-ray crystallography as the tuck-over bridging hydride species, $(C_5Me_5)_2Ln(\mu\text{-H})(\mu\text{-}\eta^1{:}\eta^5\text{-}CH_2C_5Me_4)Ln(C_5Me_5)$ (Ln = Tm, Lu), **3-Ln**, eq 5. Although the complexes were not isolated in synthetically useful yields, the result shows that C−H bond activation pathways are viable under mechanochemical conditions.

$$\cdots\ +\ KC_5Me_5\ \xrightarrow[-\ KBPh_4]{}\ \cdots \qquad (5)$$

2-Ln
Ln = Tm, Lu   **3-Ln**
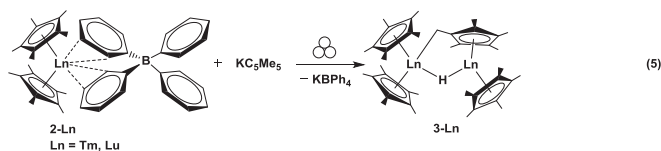
A small amount of crystals of **3-Tm** were grown from pentane in the triclinic space group, $P\bar{1}$, and the unit cell was found to be isomorphous to those of the previously reported **3-Lu** [21], **3-Sm** [20], and the heterobimetallic **3-La/Lu** analogs [18]. A low quantity of single crystals of the lutetium mechanochemical product were grown from a concentrated methylcyclohexane solution at −35 °C and, in this case, **3-Lu** crystallized in the monoclinic space group, $P2_1/n$, Fig. 1. This unit cell is different that that of the previously reported structure [21] due to the presence of methylcyclohexane in the lattice. As shown in Table 1, the difference in unit cells did not significantly affect the structural parameters.

The tuckover hydride complexes, **3-Ln**, had previously been generated from the decomposition of the bridging-hydride complexes, $[(C_5Me_5)_2Ln(\mu\text{-H})]_2$. The tuckover complexes presumably
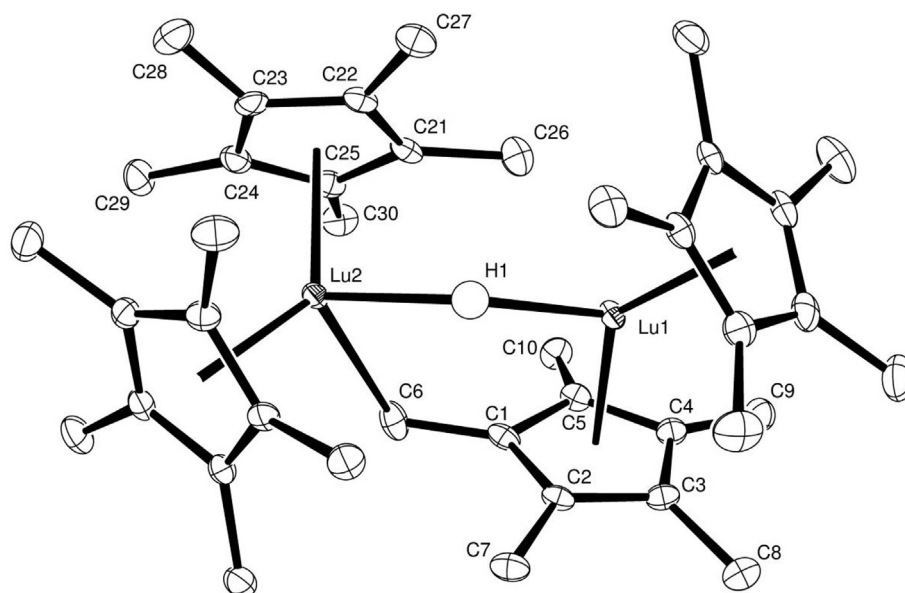

Fig. 1. Thermal ellipsoid plot of **3-Lu** drawn at 50% probability level. A methylcyclohexane molecule and hydrogen atoms, except H1, are omitted for clarity.

formed by the loss of H_2 in a conventional C—H bond activation reaction involving sigma bond metathesis between the metal hydride and the methyl C—H bond [18—21]. Since no hydrides are present in the cationic precursor, **2-Ln**, a different mode of C—H bond activation may be occurring in this case. It is conceivable that the tuckover hydride complexes **3-Ln** arise from decomposition of the target molecule, $(C_5Me_5)_3Ln$, **1-Ln**. In the previous studies of mechanochemical synthesis of the structurally characterized complexes, $(C_5Me_5)_3Ln$ (Ln = Ho and Er), **1-Ln**, according to eq 4 [17], **3-Ln** complexes were occasionally obtained as dark red-orange side products. X-ray crystallographic data on **3-Er** obtained from one of those reactions is given in the Supporting Information (Tables S6—10). $(C_5Me_5)_3Ln$ complexes are known to react as if one of the $(C_5Me_5)^{1-}$ rings was a $(\eta^1-C_5Me_5)^{1-}$ ligand, i.e., "$(C_5Me_5)_2Ln(\eta^1-C_5Me_5)$" [9]. The $(\eta^1-C_5Me_5)^{1-}$ ligand would be capable of metalating a $(C_5Me_5)^{1-}$ ring to make C_5Me_5H and $[C_5Me_4(CH_2)]^{2-}$, but the origin of the hydride ligand in **3-Ln** is more difficult to explain. Since it is now known that Lu(II) complexes exist [23] and that Ln(II) complexes can effect C—H bond activation to make hydride complexes [24,25], it is possible that the formation of **3-Ln** could proceed through $(C_5Me_5)_3Ln$-based sterically induced reduction [9,26,27] by a $(C_5Me_5)^{1-}$ ligand. However, no evidence of $(C_5Me_5)_2$, the byproduct of such a reduction, was observed. Since the mechanochemical reaction cannot be followed spectroscopically, there are no data with which to evaluate these possibilities.

For ytterbium, attempts to synthesize the cationic precursor, $(C_5Me_5)_2Yb(\mu\text{-}Ph)_2BPh_2$, by the same literature procedures [10,11] successful for other rare-earth metals led to reduction and isolation of an Yb(II) complex. Following the previously reported procedures for the synthesis of $(C_5Me_5)_2Ln(\eta^3\text{-}C_3H_5)$ complexes [10,11,28], the reaction of $(C_5Me_5)_2Yb(\mu\text{-}Cl_2)K(THF)_2$ with allyl magnesium chloride in toluene and subsequent extraction in hexane yielded the dark microcrystalline allyl complex, $(C_5Me_5)_2Yb(\eta^3\text{-}C_3H_5)$, **4**. Drying **4** further under reduced pressure at 45 °C over three days and placing a concentrated hexane solution of **4** in a −30 °C freezer gave black single crystals of **4** suitable for X-ray diffraction Fig. 2. The structural data for **4** are summarized in Table 2. These are consistent with other $(C_5Me_5)_2Ln(\eta^3\text{-}C_3H_5)$ complexes as shown [28].

Reaction of **4** with [HNEt_3][BPh_4] in toluene resulted in the formation of the Yb(II) complex, $(C_5Me_5)Yb(\mu\text{-}Ph)_2BPh_2$, **5** [22], eq 6, Fig. 3. Although this route to **5** is not synthetically useful, it shows the care that must be used with Yb(III) syntheses to avoid reduction to Yb(II) products.

The crystals of **5** were obtained from a concentrated toluene solution at −35 °C and formed in the P2$_1$/n space group with toluene in the lattice. Previously, a structure of **5** synthesized from

Table 1

Bond lengths [Å] and angles [°] of **3-Lu**, crystallized in $P2_1/n$ with methylcyclohexane in the lattice and solvent free in $P\bar{1}$ [21].

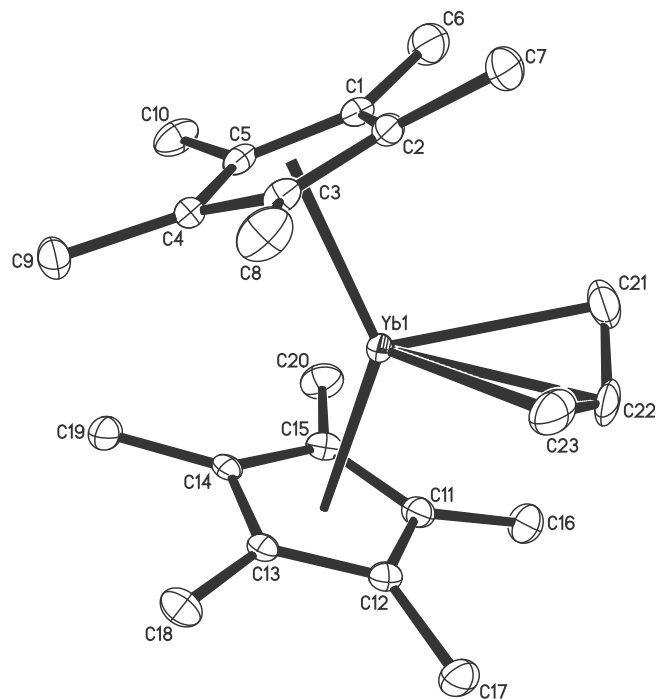|	3-Lu(MCH) $P2_1/n$	3-Lu $P\bar{1}$
Lu(1)-Cnt1[a]	2.321	2.333
Lu(1)-Cnt2	2.286	2.296
Lu(2)-Cnt3[b]	2.320	2.334
Lu(2)-Cnt4	2.347	2.344
Lu(1)−H(1)	2.06(4)	2.01(5)
Lu(2)−H(1)	2.13(4)	2.09(5)
Lu(2)−C(6)	2.548(3)	2.556(5)
Lu(1)−C(26)	2.817(4)	2.815(5)
Cnt1-Lu(1)-C(26)	106.2	105.7
Cnt2-Lu(1)-C(26)	109.5	108.8
Cnt1-Lu(1)-Cnt2	136.1	136.7
Cnt3-Lu(2)-C(6)	107.1	110.7
Cnt4-Lu(2)-C(6)	109.6	110.7
Cnt3-Lu(2)-Cnt4	133.9	134.0

[a] Cnt1 = C(1)−C(5).
[b] Cnt3 = C(21)−C(25).

Fig. 2. Thermal ellipsoid plot of **4** drawn at the 50% probability level. Hydrogen atoms are omitted for clarity.

$(C_5Me_5)_2Yb$ and [HNEt_3][BPh_4] also formed crystals in the P2$_1$/n space group [22]. In that case, however, the complex was obtained from a concentrated benzene solution and had benzene in the lattice such that the complexes are not isomorphous. Nonetheless, both have two molecules of $(C_5Me_5)Yb(\mu\text{-}Ph)_2BPh_2$ in the unit cell. As shown in Table 3, the difference in lattice solvent did not significantly affect the structural parameters.

It is interesting to note that the reduction reaction that formed **5** occurred by the addition of a Brønsted acid, [HNEt_3][BPh_4]. However, formation of Yb(II) complexes from Yb(III) complexes is known to be facile due to the −1.15 V (vs NHE) Yb^{3+}/Yb^{2+} reduction potential [30]. For example, the Yb(III) complex, $[(C_5H_4Me)_2YbMe]_2$, forms the Yb(II) complex, $(C_5H_4Me)_2Yb(THF)$, upon exposure to UV light or by heating to 80 °C [31]. Andersen and coworkers have shown that ytterbium bipyridine (bipy) complexes, $Cp^x_2Yb(bipy)$ ($Cp^x = C_5Me_5$, 1,3-$(CMe_3)_2C_5H_3$, C_5Me_4H; bipy = 2,2'-bipyridine) exist in temperature dependent equilibria as a mixture of Yb(III) $(bipy)^{1-}$ and Yb(II) neutral bipy complexes [32]. Since $[BPh_4]^{1-}$ is known to be a reductant [33—41], it is possible that this effects the reduction in eq 6. The ease in forming Yb(II) complexes suggests that if "$(C_5Me_5)_3Yb$" were formed by mechanochemistry, it might form the known $(C_5Me_5)_2Yb$ [42].

3. Conclusion

Attempts to synthesize the sterically crowded complexes, $(C_5Me_5)_3Ln$, **1-Ln**, with the smaller lanthanide metals, Tm, Yb, and Lu, by mechanochemical reaction of $(C_5Me_5)_2Ln(\mu\text{-}Ph)_2BPh_2$, **2-Ln**, and KC_5Me_5 have not been successful. The ball-milling reaction produces the tuckover hydride complexes, $(C_5Me_5)_2Ln(\mu\text{-}H)(\mu\text{-}\eta^1:\eta^5\text{-}CH_2C_5Me_4)Ln(C_5Me_5)$ (Ln = Tm, Lu), **3-Ln,** in low yields, but demonstrates that C—H bond activation reactivity can occur under these mechanochemical conditions. For ytterbium, efforts to prepare the $(C_5Me_5)_2Ln(\mu\text{-}Ph)_2BPh_2$ precursor by reaction of $(C_5Me_5)_2Yb(\eta^3\text{-}C_3H_5)$ with [HNEt_3][BPh_4] formed $(C_5Me_5)Yb(\mu\text{-}Ph)_2BPh_2$, **5**, and revealed another facile reduction route for the

Table 2
Comparison of selected bond lengths [Å] and angles [°] of Cp*$_2$Ln(η^3-C$_3$H$_5$), **4**, with other Cp*$_2$Ln(η^3-C$_3$H$_5$) complexes (Cp* = C$_5$Me$_5$). The eight coordinate ionic radii of trivalent Y, Yb and Lu are 1.019, 0.985, and 0.977 Å respectively [29].

	Cp*$_2$Y(C$_3$H$_5$) [28]	Cp*$_2$Yb(C$_3$H$_5$), **4**	Cp*$_2$Lu(C$_3$H$_5$) [28]
Ln-Cnt1[a]	2.381	2.328	2.318
Ln-Cnt2[b]	2.362	2.313	2.301
Ln-C(allyl)	2.582(2)	2.555(4)	2.549(5)
	2.582(2)	2.559(4)	2.548(5)
	2.601(2)	2.562(4)	2.545(5)
C(allyl)-C(allyl)	1.392(3)	1.381(7)	1.382(8)
	1.391(3)	1.392(7)	1.383(9)
Cnt1-Ln-Cnt2	138.8	138.1	138.5
C(allyl)-C(allyl)-C(allyl)	125.9(2)	127.2(5)	127.7(5)

[a] Cnt1 = C(1)−C(5).
[b] Cnt2 = C(11)−C(15).
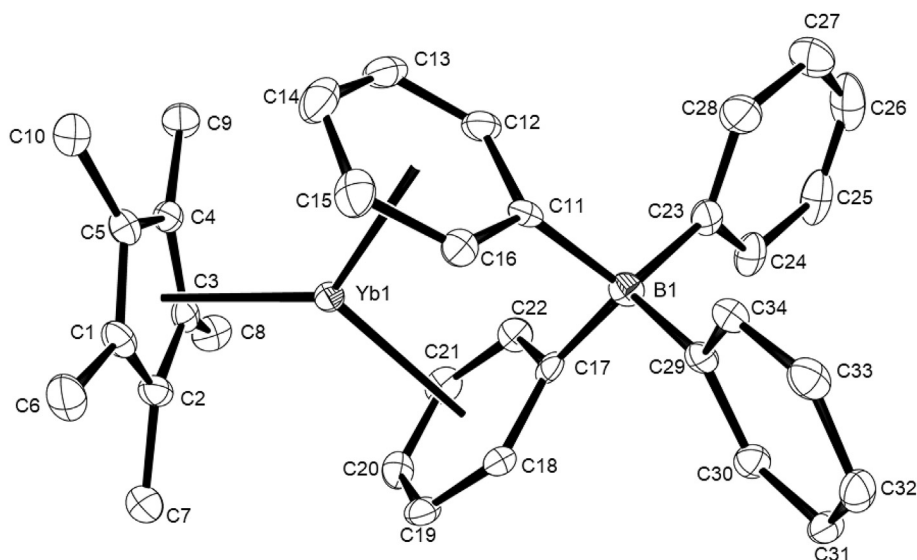
Fig. 3. Thermal ellipsoid plot of **5**. Hydrogen atoms, second (C$_5$Me$_5$)Yb(μ-Ph)$_2$BPh$_2$ unit, and two toluene molecules are omitted for clarity.

Table 3
Bond lengths [Å] and angles [°] comparison for (C$_5$Me$_5$)Yb(μ-Ph)$_2$BPh$_2$, **5**, crystallized in P2$_1$/n with toluene (this study) or benzene [22] in the lattice.

	5(toluene)	**5(benzene)** [22]
Yb(1)-Cnt1[a]	2.385	2.381 Å
Yb(1)-Cnt2[b]	2.605	2.605 Å
Yb(1)-Cnt3[c]	2.627	2.639 Å
Yb(2)-Cnt4[d]	2.395	2.382 Å
Yb(2)-Cnt5[e]	2.616	2.581 Å
Yb(2)-Cnt6[f]	2.593	2.636 Å
Cnt1-Yb(1)-Cnt2	124.1	124.7°
Cnt1-Yb(1)-Cnt3	127.0	125.8°
Cnt2-Yb(1)-Cnt3	108.1	109.5°
Cnt4-Yb(2)-Cnt5	125.6	124.2°
Cnt4-Yb(2)-Cnt6	125.6	126.0°
Cnt5-Yb(2)-Cnt6	108.1	109.7°

[a] Cnt1 = C(1)−C(5).
[b] Cnt2 = C(11)−C(16).
[c] Cnt3 = C(17)−C(22).
[d] Cnt4 = C(35)−C(42) (See SI).
[e] Cnt5 = C(45)−C(50) (See SI).
[f] Cnt6 = C(51)−C(56) (See SI).

formation of Yb(II) complexes.

4. Experimental

All manipulations and syntheses described below were conducted with the rigorous exclusion of air and water using standard Schlenk line and glovebox techniques under an argon or dinitrogen atmosphere. Solvents were sparged with UHP argon and dried by passage through columns containing Q-5 and molecular sieves prior to use. Deuterated NMR solvents were dried over NaK alloy, degassed by three freeze-pump-thaw cycles, and vacuum transferred before use. Allylmagnesium chloride and dioxane were purchased from Aldrich and used as obtained. [HNEt$_3$][BPh$_4$] [43], K(C$_5$Me$_5$) [44], and (C$_5$Me$_5$)$_2$Ln(μ-Ph)$_2$BPh$_2$ (Ln = Tm [10], Lu [45]) were prepared according to literature procedures. (C$_5$Me$_5$)$_2$Er(μ-H)(μ-η^1:η^5-CH$_2$C$_5$Me$_4$)Er(C$_5$Me$_5$), **5-Er**, was prepared serendipitously using the literature procedure for (C$_5$Me$_5$)$_3$Er [17]. ^{1}H and ^{13}C NMR spectra were obtained on a Bruker DRX500 MHz spectrometer with a TCI probe at 25 °C or a Bruker AVANCE600 MHz spectrometer with a BBO probe at 25 °C. Elemental analyses were conducted on a PerkinElmer 2400 Series II CHNS elemental analyzer. IR spectra were taken as compressed solids on a Thermo Scientific Nicolet iS5 spectrometer with an iD5 ATR attachment or with an Agilent Cary 630 FTIR spectrometer. Disperser milling was performed with an Ultra-Turrax Tube Drive and BMT-20-S tubes, both purchased from IKA.

(C$_5$Me$_5$)$_2$Yb(μ-Cl$_2$)K(THF)$_2$. In a nitrogen-filled glovebox, KC$_5$Me$_5$ (4.00 g, 22.9 mmol) was slowly added to a stirred colorless slurry of YbCl$_3$ (2.17 g, 7.78 mmol) in THF (100 mL). The reaction mixture initially turned deep blue then slowly changed color to dark maroon. After 2 d, the solution mixture was concentrated to

40 mL and centrifuged to remove insoluble material. The dark supernatant was filtered and dried under reduced pressure to give a dark maroon solid. This solid was washed using toluene (3x) and hexane (3x) over a glass filter frit, then collected and dried under reduced pressure to give the ate-salt complex, $(C_5Me_5)_2Yb(\mu\text{-}Cl_2)$ $K(THF)_2$, (3.56 g, 5.10 mmol, 66%). ^1H NMR (500 MHz, THF-d_8): δ 3.61 (t, 6H, THF), 3.27 (s, 30H, C_5Me_5), 1.77 (m, 6H, THF). ^{13}C NMR (600 MHz, THF-d_8): δ 129.47 (s, C_5Me_5), 128.71 (s, C_5Me_5), 67.71 (s, THF), 25.59 (s, THF), 11.34 (s, C_5Me_5). IR (cm^{-1}): 2903s, 2856s, 2726w, 1540 m, 1437 m, 1379 m, 1246w, 1023 m, 774s. Anal. Calcd for $C_{28}H_{46}Cl_2KO_2Yb$: C, 48.20; H, 6.65; Found: C, 44.75; H, 6.17. The found C/H ratio, $C_{28}H_{46}$, is consistent with the formula and suggests incomplete combustion [17,46–50].

$(C_5Me_5)_2Lu(\mu\text{-}H)(\mu\text{-}\eta^1\text{:}\eta^5\text{-}CH_2C_5Me_4)Lu(C_5Me_5)$, 3-Lu. In an argon-filled glovebox free of coordinating and aromatic solvents, a BMT-20-S tube was charged with $(C_5Me_5)_2Lu(\mu\text{-}Ph)_2BPh_2$ (340 mg, 0.46 mmol), KC_5Me_5 (135 mg, 0.76.6 mmol) and 40 stainless-steel balls (6 mm). The colorless mixture was milled for 40 min using an Ultra-Turrax Tube Drive (max speed setting), after which a pale orange mixture was obtained. Hexane (10 mL) was added to the mixture, followed by centrifugation to produce a dark red-orange solution which was collected in a vial. The solvent was removed under reduced pressure to give a low yield of dark orange oil. The oil was dissolved in minimal amount of methylcyclohexane and left at −35 °C for over 7 days. A small quantity of orange single crystals of $(C_5Me_5)_2Lu(\mu\text{-}H)(\mu\text{-}\eta^1\text{:}\eta^5\text{-}CH_2C_5Me_4)Lu(C_5Me_5)$, **3-Lu** [21], was obtained after several days as confirmed by X-ray diffraction.

$(C_5Me_5)_2Tm(\mu\text{-}H)(\mu\text{-}\eta^1\text{:}\eta^5\text{-}CH_2C_5Me_4)Tm(C_5Me_5)$, 3-Tm. Similar to the procedure for **3-Lu**, in an argon-filled glovebox free of coordinating and aromatic solvents, $(C_5Me_5)_2Tm(\mu\text{-}Ph)_2BPh_2$ (200 mg, 0.26 mmol) and KC_5Me_5 (46 mg, 0.26 mmol) were milled, extracted, and dried to give a low yield of orange oil. Pentane (2 mL) was added to the oil, and the resulting orange solution was filtered and stored at −35 °C. A small amount of dark orange single crystals of $(C_5Me_5)_2Tm(\mu\text{-}H)(\mu\text{-}\eta^1\text{:}\eta^5\text{-}CH_2C_5Me_4)Tm(C_5Me_5)$, **3-Tm**, were obtained after over 7 days, as confirmed by matching unit cell using X-ray diffraction.

$(C_5Me_5)_2Yb(\eta^3\text{-}C_3H_5)$, 4. In a nitrogen-filled glovebox, allyl magnesium chloride (3.0 mL of a 2.0 M THF solution) was added to a stirred maroon slurry of $(C_5Me_5)_2Yb(\mu\text{-}Cl_2)K(THF)_2$ (3.56 g, 5.10 mmol) in toluene (50 mL). No obvious color change was observed. The reaction was allowed to stir for 4 h and then volatiles were removed under reduced pressure to yield a mixture of brown and white solids. Hexane (40 mL) and dioxane (1 mL) were added and the mixture was allowed to stir. After 4 h, the mixture was centrifuged, and the solvent was removed under reduced pressure to yield $(C_5Me_5)_2Yb(\eta^3\text{-}C_3H_5)$, **4**, as black crystalline solids. The solids were dried further under reduced pressure at 45 °C over three days to give black crystalline solids of **4** (1.20 g, 2.48 mmol, 49%). Black single crystals of **4** suitable for X-ray diffraction were grown from a concentrated hexane solution at −30 °C. ^1H NMR (500 MHz, C_6D_6): δ 1.94 (s, 30H, C_5Me_5). The C_3H_5 resonances appear as broad signals at 6.16 ppm and 7.69 ppm. ^{13}C NMR (600 MHz, C_6D_6): δ 110.32 (s, C_5Me_5), 109.19 (s, C_5Me_5), 69.34 $((CH_2)_2CH)$, 66.31 $((CH_2)_2CH)$, 11.44 (s, C_5Me_5), 9.97 (s, C_5Me_5). No $(CH_2)_2CH$ resonances were observable. IR (cm^{-1}): 2903s, 2854s, 2718w, 1435 m, 1375 m, 1051s, 1020 m, 896 m. Anal. Calcd for $C_{21}H_{31}Yb$: C, 55.25; H, 6.84. The found values (54.26, 7.53), (54.21, 7.47), (55.88, 7.64), (55.92, 7.67), and (56.25, 7.62) from five different samples all have CH ratios of $C_{31}H_{34}$ (4 values) or $C_{31}H_{35}$ (1 value) which is close to the theoretical $C_{21}H_{31}$, but an exact match with the calculated values has not been obtainable [51].

$(C_5Me_5)Yb(\mu\text{-}Ph)_2BPh_2$, 5. In an argon-filled glovebox free of coordinating solvents, $[HNEt_3][BPh_4]$ (218 mg, 0.516 mmol) was slowly added to a stirred solution of $(C_5Me_5)_2Yb(\eta^3\text{-}C_3H_5)$ (250 mg,

0.516 mmol) in toluene (15 mL). The solution mixture changed from maroon to dark brown-green. The mixture was centrifuged to remove insoluble material and volatiles were removed from the solution under vacuum to yield crystalline solids of $(C_5Me_5)Yb(\mu\text{-}Ph)_2BPh_2$, **5** (280 mg, 0.447 mmol, 87%). Single crystals of **5** suitable for X-ray diffraction were grown from the toluene solution by pentane layer diffusion at −30 °C. ^1H NMR (C_6D_6): δ 7.65 (s, BPh_4), 7.13 (m, BPh_4), 7.05 (m, BPh_4), 1.67 (s, C_5Me_5) ppm. This NMR matches with that of the previously reported complex [22].

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jorganchem.2019.120885.

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