

# Synthesis, Structure, and Reactivity of the Ethyl Yttrium Metallocene, $(C_5Me_5)_2Y(CH_2CH_3)$ , Including Activation of Methane

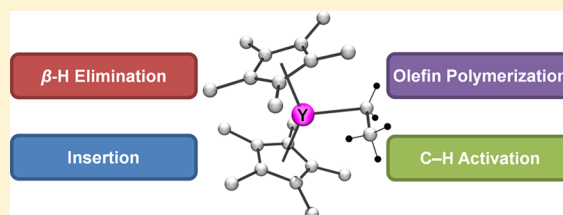
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**S** Supporting Information

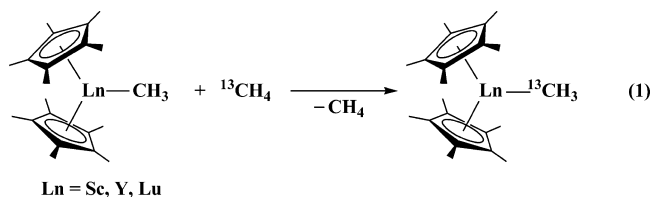
**ABSTRACT:**  $(C_5Me_5)_2Y(\mu-Ph)_2BPh_2$ , **1**, reacted with ethyllithium at  $-15^\circ C$  to make  $(C_5Me_5)_2Y(CH_2CH_3)$ , **2**, which is thermally unstable at room temperature and formed the C–H bond activation product,  $(C_5Me_5)_2Y(\mu-H)(\mu-\eta^1:\eta^5-CH_2C_5Me_4)Y(C_5Me_5)$ , **3**, containing a metalated  $(C_5Me_5)^{1-}$  ligand. Spectroscopic evidence for **2** was obtained at low temperature, and trapping experiments with  $^iPrNC-N^iPr$  and  $CO_2$  gave the Y– $CH_2CH_3$  insertion products,  $(C_5Me_5)_2Y-[^iPrNC(Et)N^iPr-\kappa^2N,N^i]$ , **4**, and  $[(C_5Me_5)_2Y(\mu-O_2CEt)]_2$ , **5**.

Although **2** is highly reactive, low temperature isolation methods allowed the isolation of single crystals which revealed an  $82.6(2)^\circ Y-CH_2-CH_3$  bond angle consistent with an agostic structure in the solid state. Complex **2** reacted with benzene and toluene to make  $(C_5Me_5)_2YPh$ , **7**, and  $(C_5Me_5)_2YCH_2Ph$ , **8**, respectively. The reaction of **2** with  $[(C_5Me_5)_2YCl]_2$  formed  $(C_5Me_5)_2Y(\mu-Cl)(\mu-\eta^1:\eta^5-CH_2C_5Me_4)Y(C_5Me_5)$  in which a  $(C_5Me_5)^{1-}$  ligand was metalated. C–H bond activation also occurred with methane which reacted with **2** to make  $[(C_5Me_5)_2YMe]_2$ , **9**.



## INTRODUCTION

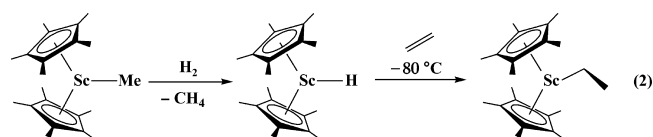
One of the most reactive forms of a metal–carbon bond is found in alkyl complexes of metallocenes of scandium, yttrium, and the lanthanides. For this reason, rare earth cyclopentadienyl/alkyl complexes continue to be heavily studied for their potential use as catalysts for a variety of molecular transformations including polymerization, hydrogenation, hydroamination, hydrosilylation, hydroboration, hydrophosphination, hydroalkoxylation, and hydrothiolation.<sup>1–7</sup> The C–H bond activation of methane by complexes such as  $(C_5Me_5)_2LnMe$  ( $Ln = Sc, Y, Lu$ ), eq 1, is the quintessential example of this



type of reactivity. Due to the high reactivity of the M–C bond with these metals, the solvent and reaction conditions must be carefully chosen to allow isolation. In addition, due to the possibility of  $\beta$ -H elimination with alkyl groups containing  $\beta$ -hydrogen atoms, research efforts have historically focused on primarily Me,  $CH_2SiMe_3$ ,  $CH(SiMe_3)_2$ , alkynyl, allyl, and aryl hydrocarbyl ligands.<sup>2,10–25</sup> Accordingly, there are few cases where ethyl complexes of these metals have been isolated or even observed.

The first examples of rare earth metallocene ethyl complexes,  $(C_5H_5)_2LnEt(THF)$  ( $Ln = Lu, Y$ )<sup>15,17</sup> and  $(C_5H_4Me)_2YEt(THF)$ ,<sup>17</sup> were THF solvates and could only be characterized by  $^1H$  NMR spectroscopy, as removal of solvent led to

decomposition. Attempts by Watson et al. to isolate an *unsolvated* lutetium metallocene ethyl complex, “ $(C_5Me_5)_2LuEt$ ”, by reacting  $(C_5Me_5)_2LuMe$  with ethane (instead of methane as shown in eq 1) resulted in a much slower formation of product, which could not be isolated due to rapid decomposition. This was attributed to  $\beta$ -H elimination although the system was too reactive to allow free ethylene or the corresponding Ln–hydride product to be observed.<sup>9</sup> With scandium, Bercaw et al. successfully isolated an *unsolvated* metallocene ethyl complex,  $(C_5Me_5)_2ScEt$ , via insertion of ethylene into the Sc–H bond of  $(C_5Me_5)_2ScH$  (made in situ from  $(C_5Me_5)_2ScMe$  and  $H_2$ ), eq 2.<sup>8</sup> Surprisingly, this



*unsolvated* ethyl complex was stable at room temperature and even in toluene. Unlike the solvated  $(C_5H_5)_2LnEt(THF)$  and  $(C_5H_4Me)_2YEt(THF)$  examples above, NMR and IR spectroscopic evidence suggested that there was an interaction between the  $\beta$ -Me and Sc in this complex and that the ethyl ligand must be bent inward toward the metal. Similar spectroscopic and even structural evidence of this  $\beta$ -agostic interaction was found in the Ti–ethyl complex,  $Ti(Me_2P-CH_2CH_2PMe_2)EtCl_3$ ,<sup>26,27</sup> and this has been analyzed theoretically.<sup>28</sup> Some scandium and yttrium nonmetallocene ethyl complexes,  $[ArNC(tBu)CHC(tBu)NAr]ScEt_2$  ( $Ar = C_6H_3^iPr_2$

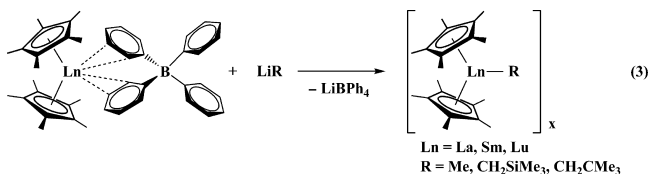
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2,6),<sup>29a</sup> [N(SiMe<sub>2</sub>CH<sub>2</sub>P<sup>i</sup>Pr<sub>2</sub>)<sub>2</sub>]ScEt<sub>2</sub>,<sup>29b</sup> and (DADMB)YEt-(THF)<sub>2</sub> (DADMB = 2,2'-bis-[(*tert*-butyl-dimethylsilyl)-amido]-6,6'-dimethylbiphenyl)<sup>30</sup> have been crystallographically characterized as well as many rare earth complexes containing bridging ethyl groups, [(μ-Et)Si(C<sub>5</sub>H<sub>4</sub>)(C<sub>5</sub>Me<sub>4</sub>)<sub>2</sub>Lu<sub>2</sub>(μ-Et)(μ-H)],<sup>31</sup> La[(μ-Et)<sub>2</sub>AlEt<sub>2</sub>]<sub>3</sub>,<sup>32</sup> {Ln[(μ-Et)<sub>3</sub>AlEt<sub>2</sub>]}<sub>μ</sub>,<sup>33</sup> Ln[(μ-Et)<sub>2</sub>-AlEt<sub>2</sub>]<sub>2</sub>(THF)<sub>2</sub>,<sup>34</sup> (C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>Sm(μ-Et)<sub>2</sub>AlEt<sub>2</sub>,<sup>35</sup> (C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>Sm-(THF)(μ-η<sup>2</sup>-Et)AlEt<sub>3</sub>,<sup>36</sup> [Me<sub>2</sub>Si(MeC<sub>9</sub>H<sub>5</sub>)<sub>2</sub>]Y(μ-Et)(μ-Me)-AlEt<sub>2</sub>,<sup>37</sup> and (Pr<sub>3</sub>C<sub>6</sub>H<sub>2</sub>CO<sub>2</sub>AlEt<sub>3</sub>)<sub>2</sub>La(μ-Et)<sub>2</sub>AlEt<sub>2</sub>.<sup>38</sup>

The Ti<sup>4+</sup> ethyl complex, Ti(Me<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>PM<sub>2</sub>)EtCl<sub>3</sub>,<sup>26,27</sup> constituted one of the first examples of agostic systems.<sup>39,40</sup> Initially, it was argued that d<sup>0</sup> complexes could not β-H eliminate because they did not have d electrons to back-donate.<sup>26</sup> Nevertheless, β-H elimination has been shown to be a viable decomposition pathway for rare earth alkyl complexes containing β-hydrogen atoms.<sup>15,16,41–44</sup> However, direct observation of this pathway for isolable complexes with the simplest of these ligands, (CH<sub>2</sub>CH<sub>3</sub>)<sup>1-</sup>, has been elusive.

Given the apparent difference in stability between (C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>ScEt and "(C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>LuEt", it was desirable to synthesize and isolate reactive ethyl complexes of rare earth metals larger than scandium to investigate their relative thermal stability, their ability to perform C–H bond activation and/or β-H elimination, and possibly their structure. One approach involves the tetraphenylborate salt of a metallocene cation, (C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>Ln(μ-Ph)<sub>2</sub>BPh<sub>2</sub>, previously shown to provide facile access to unsolvated alkyl complexes, (C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>LnR, eq 3, that



are highly reactive in C–H bond activation.<sup>45–47</sup> We report the synthesis of an ethyl complex by this route using yttrium as the metal to enhance the amount of data obtainable via NMR spectroscopy due to the diamagnetic nature of the Y<sup>3+</sup> ion and its 100% naturally abundant nuclear spin of *I* = 1/2.

## EXPERIMENTAL SECTION

The syntheses and manipulations described below were conducted under nitrogen with rigorous exclusion of air and water using Schlenk, vacuum line, and glovebox techniques. Solvents were sparged with argon and dried over columns containing Q-5 and molecular sieves. NMR solvents (Cambridge Isotope Laboratories) were dried over NaK alloy, degassed by three freeze–pump–thaw cycles, and vacuum transferred before use (with the exception of D<sub>2</sub>O, which was used as received). LiEt (Aldrich) was purchased as a 0.5 M solution in 9:1 benzene/cyclohexane and was placed under vacuum to remove the solvent before use. PrN=C=N'Pr (Aldrich) was dried over molecular sieves and degassed by three freeze–pump–thaw cycles before use. Me<sub>3</sub>SiCl (Alfa Aesar) was dried over CaH<sub>2</sub> and vacuum transferred before use. Ultrahigh purity CO<sub>2</sub> (Airgas), CH<sub>2</sub>=CH<sub>2</sub> (Airgas), H<sub>2</sub> (Praxair), CH<sub>4</sub> (Airgas), <sup>13</sup>CH<sub>4</sub> (Cambridge Isotope Laboratories), and CD<sub>4</sub> (Sigma-Aldrich) were used as received. The unsolvated metallocene complexes (C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>Y(η<sup>3</sup>-C<sub>3</sub>H<sub>5</sub>)<sup>48</sup> and (C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>Y(μ-Ph)<sub>2</sub>BPh<sub>2</sub>,<sup>49</sup> **1**, were prepared as previously described. <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR spectra were obtained on a Bruker GN500 MHz spectrometer at 25 °C or a CRYO500 MHz spectrometer at 5 °C, while <sup>13</sup>C and <sup>89</sup>Y NMR spectra were obtained on an AVANCE600 MHz spectrometer at –30 °C, unless otherwise specified, and were calibrated against the residual protio-solvent signal. IR samples were prepared as KBr pellets, and the spectra were

obtained on a Varian 1000 FT-IR spectrophotometer. Elemental analyses were performed with a PerkinElmer 2400 Series II CHNS analyzer.

(C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>YEt, **2**. In a nitrogen-filled glovebox, finely divided LiEt (22 mg, 0.61 mmol), (C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>Y(μ-Ph)<sub>2</sub>BPh<sub>2</sub>, **1**, (406 mg, 0.598 mmol), and a magnetic stir bar were added to a 100 mL Schlenk flask equipped with a custom-made cold-filtration apparatus (Supporting Information, Figure S1) containing a medium/fine frit, which was capped with a second 100 mL Schlenk flask. This apparatus was sealed and brought out of the glovebox. The apparatus was placed under high vacuum (10<sup>–5</sup> Torr) for 30 min, and then pentane (20 mL) was vacuum transferred onto the solids at –78 °C. The reaction mixture was allowed to warm to –15 °C and was stirred at this temperature for 12 h. The resulting light yellow slurry was cooled to –45 °C and filtered at this temperature to remove the white insoluble material, presumably LiBPh<sub>4</sub>. The yellow filtrate was placed under vacuum at –45 °C to remove the solvent. The resulting yellow solid residue was placed under dynamic high vacuum (10<sup>–5</sup> Torr) and slowly warmed to room temperature over 1 h. Once the yellow solids were completely dry, the apparatus was brought back into the glovebox, where the solids were collected to afford **2** as a yellow powder (92 mg, 40%). Crystals of **2** suitable for X-ray diffraction were obtained via slow evaporation of a concentrated pentane solution at –78 °C. <sup>1</sup>H NMR (C<sub>7</sub>D<sub>14</sub>, –70 °C): δ 1.88 (s, C<sub>5</sub>Me<sub>5</sub>, 30H), 0.19 (m, CH<sub>2</sub>CH<sub>3</sub>, 5H). <sup>13</sup>C{<sup>1</sup>H} NMR (C<sub>7</sub>D<sub>14</sub>, 5 °C): δ 116.0 (C<sub>5</sub>Me<sub>5</sub>), 29.5 (d, <sup>1</sup>J<sub>CH</sub> = 34.6 Hz, CH<sub>2</sub>CH<sub>3</sub>), 20.1 (CH<sub>2</sub>CH<sub>3</sub>), 10.1 (C<sub>5</sub>Me<sub>5</sub>). <sup>13</sup>C NMR (C<sub>7</sub>D<sub>14</sub>, –30 °C): δ 116.0 (C<sub>5</sub>Me<sub>5</sub>), 29.5 (t of d, <sup>1</sup>J<sub>CH</sub> = 131 Hz, <sup>1</sup>J<sub>CY</sub> = 35 Hz, CH<sub>2</sub>CH<sub>3</sub>), 20.1 (q, <sup>1</sup>J<sub>CH</sub> = 131 Hz, CH<sub>2</sub>CH<sub>3</sub>), 10.1 (q, <sup>1</sup>J<sub>CH</sub> = 125 Hz, C<sub>5</sub>Me<sub>5</sub>). <sup>89</sup>Y NMR (C<sub>7</sub>D<sub>14</sub>, –30 °C): 53 ppm. IR: 2963s, 2906s, 2857s, 2726m, 2589m, 2482m, 2426m, 2308w, 2032w, 1961w, 1778w, 1554w, 1489m, 1438s, 1417m, 1379m, 1246w, 1176w, 1061w, 1022m, 965m, 819m, 801m, 660w, 621w, 590m, 552m cm<sup>–1</sup>. Anal. Calcd for C<sub>22</sub>H<sub>35</sub>Y: C, 68.03; H, 9.08. Found: C, 67.72; H, 9.20.

(C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>Y[PrNC(Et)N'Pr-κ<sup>2</sup>N,N'], **4**. In a nitrogen-filled glovebox, a solution of LiEt in methylcyclohexane (1.3 mL, 0.067 M, 0.087 mmol) was quickly combined with a mixture of (C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>Y(μ-Ph)<sub>2</sub>BPh<sub>2</sub>, **1** (62 mg, 0.091 mmol), in methylcyclohexane (15 mL) at –35 °C. The reaction mixture was kept at –35 °C in the glovebox freezer for 2 d, during which time it was occasionally stirred. The resulting yellow solution was decanted from the white insoluble material and added to a cold stirred solution of PrN=C=N'Pr (14 μL, 0.089 mmol) in methylcyclohexane (1 mL). The yellow reaction mixture was allowed to warm to room temperature and was stirred for 18 h, during which time the solution became colorless. The solvent was removed under vacuum, and the resulting oily residues were extracted with hexane (10 mL). Removal of solvent under vacuum yielded **4** as a white powder (25 mg, 55%). Crystals of **4** suitable for X-ray diffraction were grown from a concentrated hexane solution at –35 °C. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>12</sub>): δ 3.62 (sept, <sup>3</sup>J<sub>HH</sub> = 6.0 Hz, CHMe<sub>2</sub>, 2H), 2.38 (q, <sup>3</sup>J<sub>HH</sub> = 7.5 Hz, CH<sub>2</sub>CH<sub>3</sub>, 2H), 1.94 (s, C<sub>5</sub>Me<sub>5</sub>, 30H), 1.25 (t, <sup>3</sup>J<sub>HH</sub> = 7.5 Hz, CH<sub>2</sub>CH<sub>3</sub>, 3H), 1.12 (d, <sup>3</sup>J<sub>HH</sub> = 6.0 Hz, CHMe<sub>2</sub>, 12H); (C<sub>6</sub>D<sub>6</sub>): δ 3.49 (sept, <sup>3</sup>J<sub>HH</sub> = 6.0 Hz, CHMe<sub>2</sub>, 2H), 2.19 (q, <sup>3</sup>J<sub>HH</sub> = 7.5 Hz, CH<sub>2</sub>CH<sub>3</sub>, 2H), 2.04 (s, C<sub>5</sub>Me<sub>5</sub>, 30H), 1.09 (t, <sup>3</sup>J<sub>HH</sub> = 7.5 Hz, CH<sub>2</sub>CH<sub>3</sub>, 3H), 1.10 (d, <sup>3</sup>J<sub>HH</sub> = 6.0 Hz, CHMe<sub>2</sub>, 12H). <sup>13</sup>C{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>12</sub>): δ 173.4 (NCN), 117.5 (C<sub>5</sub>Me<sub>5</sub>), 46.5 (CHMe<sub>2</sub>), 36.5 (CH<sub>2</sub>CH<sub>3</sub>), 13.7 (CH<sub>2</sub>CH<sub>3</sub>), 12.2 (C<sub>5</sub>Me<sub>5</sub>). IR: 2970s, 2854s, 2720m, 2597w, 1648w, 1470s, 1377s, 1325s, 1242s, 1202s, 1166s, 1113s, 1063s, 1040s, 978m, 933w, 795w, 775m, 702w, 610m, 548w cm<sup>–1</sup>. Anal. Calcd for C<sub>29</sub>H<sub>49</sub>N<sub>2</sub>Y: C, 67.68; H, 9.60; N, 5.44. Found: C, 67.35; H, 9.69; N, 5.30.

**Alternative Synthesis of 4.** In a nitrogen-filled glovebox, freshly isolated (C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>YEt, **2** (60 mg, 0.15 mmol), was dissolved in cold hexane (10 mL, –35 °C). To this stirred yellow solution, PrN=C=N'Pr (27 μL, 0.17 mmol) was added via syringe. The reaction solution was allowed to warm to room temperature and was stirred for 3 h, during which time it became colorless. The solution was filtered, and the solvent was removed under vacuum to yield **4** as a white solid (76 mg, 98%).

[(C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>Y(μ-O<sub>2</sub>CET)]<sub>2</sub>, **5**. As described above for the synthesis of **4**, LiEt (7.6 mg, 0.21 mmol) and (C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>Y(μ-Ph)<sub>2</sub>BPh<sub>2</sub>, **1** (161 mg,

0.237 mmol), were combined at  $-15\text{ }^{\circ}\text{C}$  to produce a yellow solution of **2**. This solution was exposed to 1 atm of  $\text{CO}_2$  at  $-78\text{ }^{\circ}\text{C}$ , and a colorless mixture resulted. The mixture was degassed by three freeze–pump–thaw cycles and brought into the glovebox. The supernatant was decanted, and the white precipitate was dried under vacuum to yield **5** as a white solid (66 mg, 73%).  $^1\text{H NMR}$  ( $\text{C}_6\text{D}_6$ ):  $\delta$  2.26 (q,  $^3J_{\text{HH}} = 7.5\text{ Hz}$ ,  $\text{CH}_2\text{CH}_3$ , 2H), 2.04 (s,  $\text{C}_5\text{Me}_5$ , 30H), 1.10 (t,  $^3J_{\text{HH}} = 7.5\text{ Hz}$ ,  $\text{CH}_2\text{CH}_3$ , 3H). IR: 2975m, 2910s, 2861s, 2722m, 2358w, 1959w, 1583s, 1465m, 1428s, 1376m, 1319w, 1302m, 1105w, 1079m, 1018m, 950w, 888m, 807m, 728w, 669m, 634m, 592m  $\text{cm}^{-1}$ . Anal. Calcd for  $\text{C}_{46}\text{H}_{70}\text{O}_4\text{Y}_2$ : C, 63.88; H, 8.16. Found: C, 63.56; H, 8.34.

**LiO<sub>2</sub>CEt.** In a nitrogen-filled glovebox, a 100 mL side arm sealable Schlenk flask equipped with a greaseless stopper was charged with a solution of LiEt (65 mg, 1.8 mmol) in hexane (20 mL). The flask was sealed, brought out of the glovebox, and attached to a high vacuum line. The solution was cooled to  $-78\text{ }^{\circ}\text{C}$  and degassed by briefly pulling vacuum three times. 1 atm of  $\text{CO}_2$  was introduced, and the mixture was allowed to warm to room temperature over 1 h while stirring, during which time a white solid precipitated. The mixture was degassed by three freeze–pump–thaw cycles, and the flask was brought into the glovebox. The solids were collected via centrifugation and dried under vacuum to yield  $\text{LiO}_2\text{CEt}$  as a white solid (116 mg, 85%).  $^1\text{H NMR}$  ( $\text{D}_2\text{O}$ ):  $\delta$  2.20 (q,  $^3J_{\text{HH}} = 7.5\text{ Hz}$ ,  $\text{CH}_2\text{CH}_3$ , 2H), 1.07 (t,  $^3J_{\text{HH}} = 7.5\text{ Hz}$ ,  $\text{CH}_2\text{CH}_3$ , 3H).

**Synthesis of 5 from 1 and LiO<sub>2</sub>CEt.** ( $\text{C}_5\text{Me}_5$ )<sub>2</sub>Y( $\mu\text{-Ph}$ )<sub>2</sub>BPh<sub>2</sub>, **1** (500 mg, 0.740 mmol), was added to a slurry of  $\text{LiO}_2\text{CEt}$  (56 mg, 0.74 mmol) in benzene (20 mL). The colorless reaction mixture was allowed to stir at room temperature for 2 d. The mixture was centrifuged to collect the supernatant. The solids were stirred in toluene and centrifuged, and the combined supernatants were evaporated to dryness under vacuum. The resulting white solids were stirred in hot hexane/toluene (9:1, 20 mL), and the mixture was filtered. The solvent was removed from the colorless filtrate under vacuum to yield **5** as a colorless crystalline solid (268 mg, 84%). Crystals of **5** suitable for X-ray diffraction were obtained from a concentrated toluene solution at  $-35\text{ }^{\circ}\text{C}$ .

**(C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>YPh, 7.** In a nitrogen-filled glovebox, freshly isolated ( $\text{C}_5\text{Me}_5$ )<sub>2</sub>YEt, **2** (16 mg, 0.041 mmol), was dissolved in benzene (4 mL) and stirred for 1 h, during which time the solution changed from yellow to pale yellow. The solvent was removed under vacuum, and the resulting pale yellow oily residue was found to contain **7** as the only organometallic product by  $^1\text{H NMR}$  spectroscopy.<sup>50</sup>

**(C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>YCH<sub>2</sub>Ph, 8.** In a nitrogen-filled glovebox, freshly isolated ( $\text{C}_5\text{Me}_5$ )<sub>2</sub>YEt, **2** (15 mg, 0.039 mmol), was dissolved in toluene (4 mL) and the yellow solution was stirred for 6 h, during which time no color change was observed. The solvent was removed under vacuum, and the resulting yellow oil was found to contain **8**, as well as two other major organometallic products by  $^1\text{H NMR}$  spectroscopy.<sup>50</sup> The resonances of the unidentified products are consistent with the ring-metalated isomers, “( $\text{C}_5\text{Me}_5$ )<sub>2</sub>Y( $m\text{-C}_6\text{H}_5\text{Me}$ )” and “( $\text{C}_5\text{Me}_5$ )<sub>2</sub>Y( $p\text{-C}_6\text{H}_5\text{Me}$ )”.

**Reaction of 2 with CH<sub>4</sub>.** In a nitrogen-filled glovebox, freshly isolated ( $\text{C}_5\text{Me}_5$ )<sub>2</sub>YEt, **2** (25 mg, 0.064 mmol), solids were sealed in a J-Young NMR tube and brought out of the glovebox. Methylcyclohexane-*d*<sub>14</sub> (0.5 mL) was vacuum transferred onto the solids at  $-196\text{ }^{\circ}\text{C}$ , and they were allowed to dissolve at  $-78\text{ }^{\circ}\text{C}$ . 1 atm of  $\text{CH}_4$  was then added to the NMR tube at this temperature. The sample was stored at room temperature and shaken periodically. The reaction was monitored by  $^1\text{H NMR}$  spectroscopy over 3 days. [ $(\text{C}_5\text{Me}_5)_2\text{YMe}$ ]<sub>2</sub>, **9**, was identified in the  $^1\text{H NMR}$  spectrum by a broad singlet at  $-1.25\text{ ppm}$  (see below). Other products including ethane, ( $\text{C}_5\text{Me}_5$ )<sub>2</sub>Y( $\mu\text{-H}$ )( $\mu\text{-}\eta^1\text{-}\eta^2\text{-CH}_2\text{C}_5\text{Me}_4$ )Y( $\text{C}_5\text{Me}_5$ ), **3**, and unidentified alkenes were also present in the  $^1\text{H NMR}$  spectrum. When the same experiment was performed with  $^{13}\text{CH}_4$ , the isotopically labeled [ $(\text{C}_5\text{Me}_5)_2\text{Y}^{13}\text{CH}_3$ ]<sub>2</sub>, **9**,  $^{13}\text{C}$ , was produced, as identified by the doublet at  $-1.25\text{ ppm}$  ( $^1J_{\text{CH}} = 115\text{ Hz}$ ) in the  $^1\text{H NMR}$  spectrum. When this reaction was performed with  $\text{CD}_4$ , a  $\text{C}_5\text{Me}_5$  resonance consistent with [ $(\text{C}_5\text{Me}_5)_2\text{YCD}_3$ ]<sub>2</sub> was observed in the  $^1\text{H NMR}$  spectrum as well as a multiplet at  $-1.27\text{ ppm}$  in the  $^2\text{H NMR}$  spectrum consistent with the  $\text{CD}_3$  group in this compound.

**[(C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>YMe]<sub>2</sub>, 9.** In a nitrogen-filled glovebox, LiMe (5.4 mg, 0.25 mmol) and ( $\text{C}_5\text{Me}_5$ )<sub>2</sub>Y( $\mu\text{-Ph}$ )<sub>2</sub>BPh<sub>2</sub>, **1** (153 mg, 0.23 mmol), were combined and stirred in methylcyclohexane (20 mL) over 2 d. The resulting light yellow slurry was centrifuged to remove the white solids, presumably  $\text{LiBPh}_4$ . The light yellow supernatant was filtered, and the solvent was removed under vacuum. The residue was extracted with hexane (2 mL), and the solvent was removed under vacuum to yield **9** as a yellow solid as determined by  $^1\text{H NMR}$  spectroscopy<sup>9</sup> (42 mg, 49%).  $^1\text{H NMR}$  ( $\text{C}_7\text{D}_{14}$ ):  $\delta$  1.93 (s,  $\text{C}_5\text{Me}_5$ , 30H),  $-1.25$  (br s, YMe, 3H).

**[(C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>YCl]<sub>2</sub>, 11.** In a nitrogen-filled glovebox, a solution of  $\text{Me}_3\text{SiCl}$  (72 mg, 0.66 mmol) in hexane (5 mL) was added dropwise to a stirred solution of ( $\text{C}_5\text{Me}_5$ )<sub>2</sub>Y( $\eta^3\text{-C}_3\text{H}_5$ ) (263 mg, 0.657 mmol) in hexane (10 mL). The yellow solution became a colorless suspension over 30 min. The mixture was centrifuged to collect the solids, which were rinsed with hexane (10 mL) and dried under vacuum to yield **11** as a white powder as determined by  $^1\text{H NMR}$  spectroscopy<sup>52</sup> (235 mg, 91%).

**Reaction of 2 with 11.** In a nitrogen-filled glovebox, a cold ( $-35\text{ }^{\circ}\text{C}$ ) solution of ( $\text{C}_5\text{Me}_5$ )<sub>2</sub>YEt, **2** (30 mg, 0.077 mmol), in methylcyclohexane (2 mL) was added dropwise to a stirred, heated solution of [ $(\text{C}_5\text{Me}_5)_2\text{YCl}$ ]<sub>2</sub>, **11** (101 mg, 0.128 mmol), in methylcyclohexane (10 mL). The solution immediately turned orange in color, and the solvent was removed under vacuum to yield an orange oil, which was found to contain ( $\text{C}_5\text{Me}_5$ )<sub>2</sub>Y( $\mu\text{-H}$ )( $\mu\text{-}\eta^1\text{-}\eta^2\text{-CH}_2\text{C}_5\text{Me}_4$ )Y( $\text{C}_5\text{Me}_5$ ), **3**,<sup>50,51</sup> and ( $\text{C}_5\text{Me}_5$ )<sub>2</sub>Y( $\mu\text{-Cl}$ )( $\mu\text{-}\eta^1\text{-}\eta^2\text{-CH}_2\text{C}_5\text{Me}_4$ )Y( $\text{C}_5\text{Me}_5$ ), **10**,<sup>53</sup> as well as many other unidentified products by  $^1\text{H NMR}$  spectroscopy.

**Reaction of 3 with 11.** In a nitrogen-filled glovebox, a solution of ( $\text{C}_5\text{Me}_5$ )<sub>2</sub>Y( $\mu\text{-H}$ )( $\mu\text{-}\eta^1\text{-}\eta^2\text{-CH}_2\text{C}_5\text{Me}_4$ )Y( $\text{C}_5\text{Me}_5$ ), **3**, in methylcyclohexane (2 mL) was added to a stirred boiling solution of [ $(\text{C}_5\text{Me}_5)_2\text{YCl}$ ]<sub>2</sub>, **11**, in methylcyclohexane (5 mL) for 10 min. The solvent was removed under vacuum to yield a tacky orange residue, which was found to consist of **3**,<sup>50,51</sup> **10**,<sup>53</sup> and **11**<sup>52</sup> by  $^1\text{H NMR}$  spectroscopy.

**Reaction of 2 with H<sub>2</sub>.** In a nitrogen-filled glovebox, solid ( $\text{C}_5\text{Me}_5$ )<sub>2</sub>YEt, **2** (12 mg, 0.031 mmol), was sealed in a J-Young NMR tube and brought out of the glovebox. Methylcyclohexane-*d*<sub>14</sub> (0.5 mL) was vacuum transferred onto the solids at  $-196\text{ }^{\circ}\text{C}$ , and they were allowed to dissolve at  $-78\text{ }^{\circ}\text{C}$ . 1 atm of  $\text{H}_2$  was then added to the NMR tube at this temperature. The sample was shaken and was stored at  $0\text{ }^{\circ}\text{C}$ . The solution was periodically monitored by  $^1\text{H NMR}$  spectroscopy at  $0\text{ }^{\circ}\text{C}$ , and after 15 h, nearly complete conversion to [ $(\text{C}_5\text{Me}_5)_2\text{YH}$ ]<sub>2</sub>, **6**, and ethane (0.85 ppm) was observed, along with the formation of **3**,<sup>50,51</sup> as a minor side product (<5%).

**Reaction of 2 with CH<sub>2</sub>=CH<sub>2</sub>.** In a nitrogen-filled glovebox, freshly isolated ( $\text{C}_5\text{Me}_5$ )<sub>2</sub>YEt, **2** (26 mg, 0.067 mmol), solids were sealed in a J-Young NMR tube and brought out of the glovebox. Methylcyclohexane-*d*<sub>14</sub> (0.5 mL) was vacuum transferred onto the solids at  $-196\text{ }^{\circ}\text{C}$ , and they were allowed to dissolve at  $-78\text{ }^{\circ}\text{C}$ . 1 atm of ethylene was then added to the NMR tube at this temperature. Over the course of 30 min, a white precipitate formed until there was a plug of white solid. A larger scale reaction similarly produced a white solid that starts melting at  $140\text{ }^{\circ}\text{C}$  and has a  $^1\text{H NMR}$  resonance at 1.38 ppm in tetrachloroethane-*d*<sub>2</sub> consistent with polyethylene.<sup>54</sup>

**X-ray Data Collection, Structure Determination, and Refinement.** Crystallographic details for compounds **2**, **4**, and **5** are summarized in Tables 1–4 and in the Supporting Information.

## RESULTS AND DISCUSSION

**Reaction of LiEt with ( $\text{C}_5\text{Me}_5$ )<sub>2</sub>Y( $\mu\text{-Ph}$ )<sub>2</sub>BPh<sub>2</sub>, 1.** Initial attempts to synthesize an unsolvated yttrium ethyl complex involved the reaction of **1** with LiEt in nonaromatic hydrocarbon solvents such as hexane, cyclohexane, and methylcyclohexane due to the tendency of reactive Ln–alkyl and Ln–hydride complexes to react with arenes.<sup>3,8,9,14,46,47,50,55,56</sup> In each of these three solvents, the initial white mixture started to turn yellow within minutes at room temperature and continued to turn darker in color until a dark

**Table 1. X-ray Data Collection Parameters for  $(C_5Me_5)_2YEt$ , **2**,  $(C_5Me_5)_2Y[{}^iPrNC(Et)N^iPr-\kappa^2N,N']$ , **4**, and  $[(C_5Me_5)_2Y(\mu-O_2CEt)]_2$ , **5****

	<b>2</b>	<b>4</b>	<b>5</b>
Empirical formula	$C_{22}H_{35}Y$	$C_{29}H_{49}N_2Y$	$C_{23}H_{35}O_2Y$
Fw	388.41	514.61	432.42
Temp (K)	143(2)	93(2)	88(2)
Crys syst	Monoclinic	Monoclinic	Triclinic
Space group	$P2_1/n$	$P2_1/n$	$P\bar{1}$
<i>a</i> (Å)	8.5822(8)	10.2036(4)	9.5104(10)
<i>b</i> (Å)	14.0989(13)	25.8627(10)	10.7672(12)
<i>c</i> (Å)	17.4406(17)	10.8916(4)	12.0235(13)
$\alpha$ (deg)	90	90	73.4204(13)
$\beta$ (deg)	101.9057(13)	101.0979(5)	80.3740(13)
$\gamma$ (deg)	90	90	69.1578(12)
volume (Å <sup>3</sup> )	2064.9(3)	2820.46(19)	1099.8(2)
<i>Z</i>	4	4	2
$\rho_{calcd}$ (Mg/m <sup>3</sup> )	1.249	1.212	1.306
$\mu$ (mm <sup>-1</sup> )	2.823	2.085	2.664
$R1^a$ ( $I > 2.0\sigma(I)$ )	0.0375	0.0260	0.0507
wR2 (all data) <sup>a</sup>	0.0851	0.0630	0.1316

<sup>a</sup>Definitions:  $R1 = \sum ||F_o| - |F_c|| / \sum |F_o|$ ,  $wR2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)]^{1/2}$ .

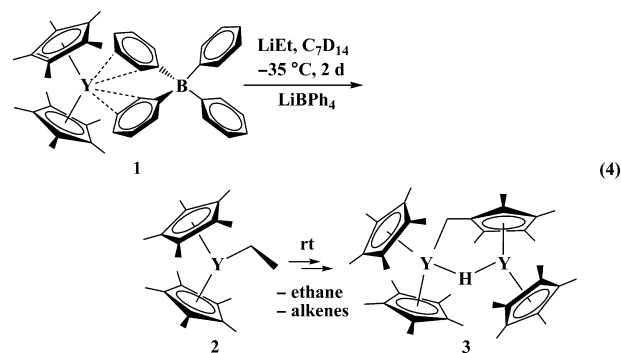
red-orange mixture remained after several hours. The red-orange product of the reaction was identified to be  $(C_5Me_5)_2Y(\mu-H)(\mu-\eta^1:\eta^5-CH_2C_5Me_4)Y(C_5Me_5)$ , **3**, by <sup>1</sup>H NMR spectroscopy.<sup>50,51</sup> This product evidently formed by C–H bond activation of a methyl group of a  $(C_5Me_5)^{1-}$  ligand to make a  $(\mu-\eta^1:\eta^5-CH_2C_5Me_4)^{2-}$  dianion that bridges between the two metals in a tuck-over fashion.

**Low Temperature NMR Characterization.** A low temperature reaction of **1** with LiEt in methylcyclohexane-*d*<sub>14</sub> at –35 °C produced a yellow mixture over 2 days of periodic stirring. The cold yellow mixture was quickly filtered into a J-Young NMR tube and the yellow solution was probed by <sup>1</sup>H NMR spectroscopy at –70 °C. The <sup>1</sup>H NMR spectrum contained a singlet at 1.88 ppm and an unresolved multiplet at 0.19 ppm that were consistent with two  $(C_5Me_5)^{1-}$  ligands and one  $(Et)^{1-}$  ligand. The <sup>13</sup>C{<sup>1</sup>H} NMR spectrum showed singlets at 116.0 and 10.1 ppm corresponding to the  $(C_5Me_5)^{1-}$  ligands, as well as a doublet ( $J_{CY} = 34.6$  Hz) at 29.5 ppm and a singlet at 20.1 ppm. The latter two peaks, which were assigned as ethyl carbons (where the methylene carbon is coupled to the  $I = 1/2$  nucleus of yttrium), were correlated to the 5H multiplet at 0.19 ppm in the <sup>1</sup>H spectrum in a 2D HMQC experiment. This indicated that the multiplet was indeed due to all five ethyl protons and that the yellow compound can be formulated as  $[(C_5Me_5)_2YEt]_n$ , **2**. The proton coupled <sup>13</sup>C NMR spectrum contained a triplet of doublets for the methylene carbon at 29.5 ppm with  $J_{CH} = 131$  Hz (and  $J_{CY} = 35$  Hz) and a quartet for the methyl carbon at 20.1 ppm with  $J_{CH} = 120$  Hz. The <sup>89</sup>Y NMR spectrum of **2** had a resonance at 53 ppm that was within the wide range (–375 to 895 ppm) found for organometallic yttrium complexes.<sup>57–59</sup> In comparison,  $(C_5Me_5)_2Y[CH-(SiMe_3)_2]$  resonates at 78.9 ppm.<sup>60</sup> A <sup>1</sup>H–<sup>89</sup>Y HMBC experiment was performed and showed the expected cross peak between the <sup>89</sup>Y resonance and the overlapped proton resonances of the ethyl group. Addition of THF to **2** in methylcyclohexane-*d*<sub>14</sub> gave a spectrum consistent with a THF adduct,  $(C_5Me_5)_2YEt(THF)$ , with the  $C_5Me_5$  resonance shifted from 1.88 to 1.89 ppm and the multiplet from the ethyl group

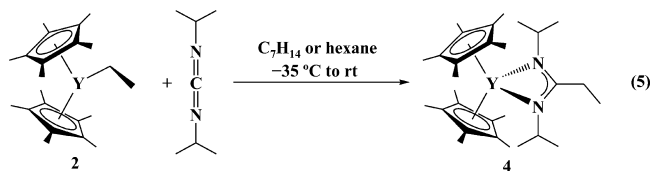
separated into a quartet of doublets at 0.10 ppm for the methylene protons ( ${}^3J_{HH} = 8$  Hz;  ${}^2J_{YH} = 2$  Hz) and a triplet at 0.37 ppm ( ${}^3J_{HH} = 8$  Hz) for the methyl protons, which reinforces the assignments above. This THF adduct was not stable overnight, however.

It is unusual for the CH<sub>2</sub> and CH<sub>3</sub> protons of an ethyl group to have similar chemical shifts such that their resonances overlap. For instance, the ethyl resonances in  $(C_5H_5)_2LuEt(THF)$ <sup>15</sup> and  $(C_5H_4Me)_2YEt(THF)$ <sup>17</sup> are separated by 1.6 ppm in both cases. In contrast, the same pair of ethyl resonances in  $(C_5Me_5)_2ScEt$ <sup>8</sup> and  $Ti(Me_2PCH_2CH_2PMe_2)EtCl_3$ ,<sup>26</sup> which were claimed to have  $\beta$ -agostic structural features, were only 0.1 and 0–0.2 ppm apart (depending on temperature), respectively. Therefore, the NMR spectroscopic data of **2** suggested that an  $Y \cdots H_3C$  agostic interaction is likely to be present in this complex as well. The weaker 120 Hz  ${}^1J_{CH}$  coupling constant for the methyl protons compared to  ${}^1J_{CH} = 131$  Hz for the methylene protons is consistent with this.<sup>8,39,40,61,62</sup>

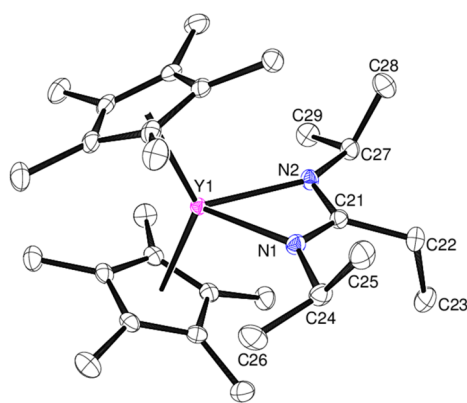
When the yellow methylcyclohexane-*d*<sub>14</sub> solution of **2** was warmed to room temperature, the same red-orange yttrium tuck-over hydride product, **3**, was identified in the <sup>1</sup>H NMR spectrum after 6 h, along with ethane (0.85 ppm) and resonances consistent with other alkenes, eq 4.



**Trapping Experiments.** Since isolation of **2** was complicated by thermal instability, efforts were made to form a thermally stable compound containing the ethyl fragment, which could be fully characterized as chemical evidence that an  $Y-Et$  unit was present. Given the many examples of carbodiimide insertions into metal–carbon bonds to form stable amidinate complexes,<sup>63–74</sup>  ${}^iPrN=C=N^iPr$  was used as a trapping reagent. A yellow solution of **2** resulting from the reaction of **1** and LiEt at –35 °C was quickly filtered and reacted with 1 equiv of  ${}^iPrN=C=N^iPr$ . The solution faded and removal of the solvent left a white powder, which was found to be the thermally stable  $(C_5Me_5)_2Y[{}^iPrNC(Et)N^iPr-\kappa^2N,N']$ , **4**, by NMR and IR spectroscopy, elemental analysis, and single crystal X-ray diffraction, eq 5.



The structure of **4**, Figure 1, shows an amidinate ligand with an ethyl fragment on the carbon backbone: a product of formal insertion of the carbodiimide into an  $Y-Et$  bond. The structural parameters are very similar to the previously reported



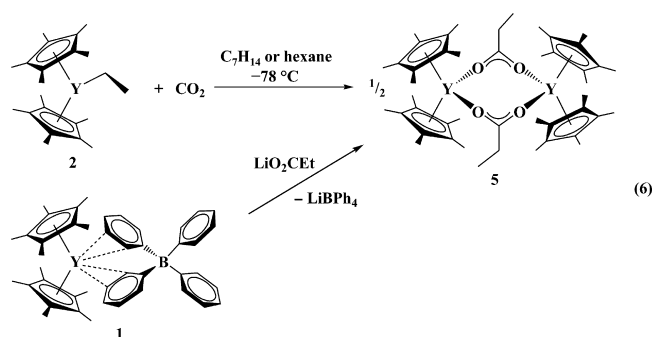
**Figure 1.** Molecular structure of  $(C_5Me_5)_2Y[PrNC(Et)N'Pr-\kappa^2N,N']$ , **4**, with thermal ellipsoids drawn at the 50% probability level and hydrogen atoms omitted for clarity.

yttrium metallocene amidinate complex,  $(C_5Me_5)_2Y[{}^tBuNC-(C\equiv CPh)N{}^tBu-\kappa^2N,N']$ ,<sup>75</sup> as summarized in Table 2.

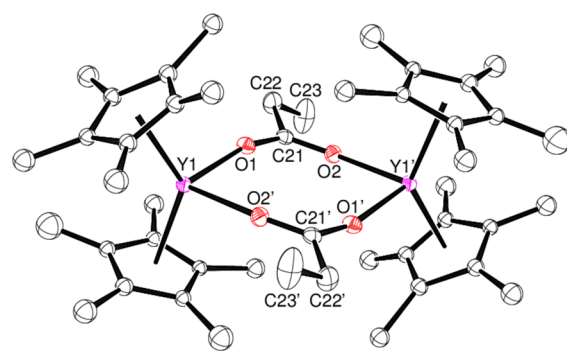
**Table 2. Selected Bond Lengths (Å) and Angles (deg) for  $(C_5Me_5)_2Y[{}^tPrNC(Et)N'Pr-\kappa^2N,N']$ , **4**, and  $(C_5Me_5)_2Y[{}^tBuNC(C\equiv CPh)N{}^tBu-\kappa^2N,N']$ <sup>75</sup>**

	<b>4</b>	$(C_5Me_5)_2Y[{}^tBuNC(C\equiv CPh)N{}^tBu-\kappa^2N,N']$
Y–Cnt	2.388	2.397
	2.415	2.427
Y–N		2.427
		2.409
	2.3398(12)	2.3643(14)
	2.3630(12)	2.3811(14)
		2.3841(14)
Y–C(NCN)		2.3833(14)
	2.7688(14)	–
	1.3357(19)	1.338(2)
	1.3402(19)	1.336(2)
		1.332(2)
Cnt–Ln–Cnt		1.339(2)
	134.3	132.1
		133.0
N–Y–N		57.15(5)
	57.42(4)	56.87(5)
		116.20(15)
N–C–N		116.40(15)
	115.19(13)	

Similarly,  $CO_2$ , which is isoelectronic with  ${}^tPrN=C=N{}^tPr$ , was reacted with solutions of **2** at  $-78\text{ }^\circ\text{C}$  to produce a colorless solution from which a white powder could be isolated. NMR spectroscopy suggested a new product containing an ethyl fragment had formed since there was the signature triplet and quartet in the  ${}^1H$  NMR spectrum. The IR spectrum of this white solid showed absorptions at  $1583$  and  $1428\text{ cm}^{-1}$ , which are within the range for OCO asymmetric and symmetric stretching frequencies, respectively, in metal carboxylate complexes<sup>71,76–87</sup> and are similar to the previously reported  $[(C_5Me_5)_2Sm(\mu-O_2CR)]_2$  complexes [R =  $CH_2CH=CH_2$  ( $1571, 1415\text{ cm}^{-1}$ ),<sup>86</sup>  $CH_2CH=CHMe$  ( $1578, 1417\text{ cm}^{-1}$ ),<sup>86</sup>  $CH_2CH=CHEt$  ( $1572, 1419\text{ cm}^{-1}$ ),<sup>86</sup>  $C_6H_5$  ( $1552, 1400\text{ cm}^{-1}$ ),<sup>86</sup>  $C_6H_5Me-m$  ( $1571, 1401\text{ cm}^{-1}$ ),<sup>46</sup>  $CH_2C_6H_5$  ( $1567, 1498\text{ cm}^{-1}$ )<sup>46</sup>]. The same white product could be synthesized by reacting **1** with  $LiO_2CEt$ , eq 6, which confirmed that a  $CO_2$



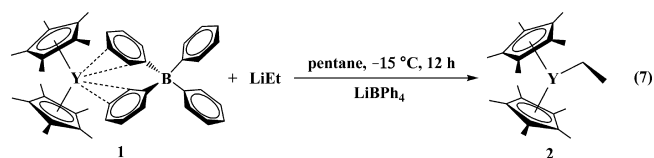
insertion product was formed. A single crystal X-ray diffraction study revealed this product to be the yttrium ethylcarboxylate dimer,  $[(C_5Me_5)_2Y(\mu-O_2CET)]_2$ , **5**, eq 6. The structure of **5**, Figure 2, shows two yttrium atoms bridged by crystallo-



**Figure 2.** Molecular structure of  $[(C_5Me_5)_2Y(\mu-O_2CET)]_2$ , **5**, with thermal ellipsoids drawn at the 50% probability level and hydrogen atoms omitted for clarity.

graphically equivalent  $(O_2CET)^{1-}$  ligands in a structure similar to those of the  $[(C_5Me_5)_2Sm(\mu-O_2CR)]_2$  complexes listed above when the difference in metal ionic radii is considered, as shown in Table 3.

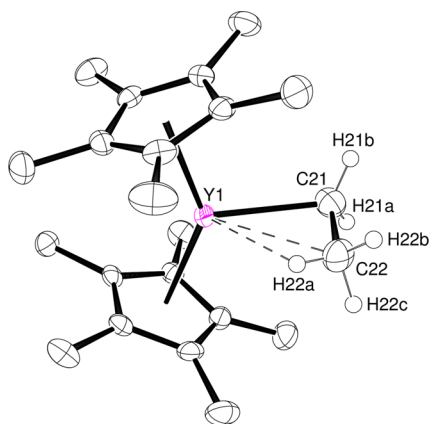
**Structural Characterization.** Encouraged by the spectroscopic and chemical evidence supporting the existence of **2**, attempts were made to isolate it using a more volatile solvent since workup would require low temperatures to prevent decomposition to **3**. In pentane, **1** reacted with  $LiEt$  at  $-15\text{ }^\circ\text{C}$  over 12 h to form a light yellow slurry, which was filtered at  $-45\text{ }^\circ\text{C}$  using a custom-made Schlenk cold-filtration apparatus (see Supporting Information, Figure S1) to give a yellow solution. The pentane was removed under vacuum at  $-45\text{ }^\circ\text{C}$ , and the product was dried further under high vacuum ( $10^{-5}$  Torr) to yield analytically pure **2** as a yellow solid in 40% yield, eq 7. Fortunately, complex **2** does not decompose as quickly in the solid state at room temperature, as long as it is completely dry.



X-ray quality crystals of **2** were eventually obtained by slow evaporation of a concentrated pentane solution at  $-78\text{ }^\circ\text{C}$ . The structure of **2**, Figure 3, shows the ethyl ligand is indeed bent inward toward the coordinatively unsaturated yttrium center,

**Table 3. Selected Bond Lengths (Å) and Angles (deg) for  $[(C_5Me_5)_2Y(\mu-O_2C_2Et)]_2$ , **5**, and  $[(C_5Me_5)_2Sm(\mu-O_2CR)]_2$  Complexes<sup>46,86</sup> {R = CH<sub>2</sub>CH=CH<sub>2</sub>, C<sub>6</sub>H<sub>5</sub>, and CH<sub>2</sub>C<sub>6</sub>H<sub>5</sub>}**

	<b>5</b>	$[(C_5Me_5)_2Sm(\mu-O_2CR)]_2$		
		R = CH <sub>2</sub> CH=CH <sub>2</sub>	C <sub>6</sub> H <sub>5</sub>	CH <sub>2</sub> C <sub>6</sub> H <sub>5</sub>
Ln–Cnt	2.430	–	–	2.449
	2.371	–	–	2.444
Ln–O	2.228(2)	2.327(2)	2.303(4)	2.303(2)
	2.252(2)	2.307(2)	2.317(4)	2.333(3)
C–O	1.256(4)	1.257(3)	1.265(6)	1.263(4)
	1.261(4)	1.252(3)	1.252(6)	1.256(4)
C(O <sub>2</sub> C)–C(R)	1.515(5)	1.518(3)	1.492(7)	1.515(5)
Cnt–Ln–Cnt	134.2	133.4	133.1	133.5
O–Ln–O	88.56(9)	90.85(7)	87.36(13)	88.95(9)
O–C–O	124.9(3)	124.5(2)	124.4(5)	124.7(3)



**Figure 3.** Molecular structure of  $(C_5Me_5)_2YEt$ , **2**, with thermal ellipsoids drawn at the 50% probability level and non-ethyl hydrogen atoms omitted for clarity.

with an Y1–C21–C22 bond angle of 82.6(2)°. This is significantly smaller than the 109.5° angle expected about an  $sp^3$  carbon and is similar to that observed in the structure of the  $\beta$ -agostic titanium ethyl complex,  $Ti(Me_2PCH_2CH_2PMe_2)EtCl_3$ ,<sup>26,27</sup> which had a Ti–CH<sub>2</sub>–CH<sub>3</sub> bond angle of 86.3(6)°. The protons on the ethyl ligand of **2** were located and refined. The possibility that C21 and C22 belong to a  $(CH=CH_2)^{-}$  ligand or perhaps two  $(Me)^{-}$  ligands disordered over two positions was not supported by the X-ray data. One of the CH<sub>3</sub> protons, H22a, was found to be oriented toward the yttrium, which is archetypal for agostic interactions,<sup>39,40</sup> and displays the intermediate geometry required prior to a  $\beta$ -H elimination process. The Y1⋯C22 and Y1⋯H22a lengths are 2.682(4) and 2.27(3) Å, respectively. The Y1–C21 bond length of 2.419(3) Å is slightly shorter than the 2.468(7) and 2.484(6) Å Y–C bond lengths in  $(C_5Me_5)_2Y[CH(SiMe_3)_2](THF)$ <sup>24</sup> and  $(C_5Me_5)_2Y(CH_2Ph)(THF)$ ,<sup>88</sup> respectively. This difference is consistent with the fact that **2** has a smaller alkyl group and smaller coordination number than these previously reported yttrium metallocene alkyl THF solvates.  $(C_5Me_5)_2Y(Me)(THF)$  has a 2.44(2) Å Y–C bond.<sup>89</sup> Selected metrical parameters for **2** are summarized in Table 4.

Once **2** could be isolated as a solid, it was analyzed by IR spectroscopy. Three medium absorptions at 2589, 2482, and 2426  $cm^{-1}$  were observed (in addition to absorptions at 2857–2963  $cm^{-1}$ ) which are significantly lower in energy than the 2850–3000  $cm^{-1}$  range of typical CH<sub>3</sub> and CH<sub>2</sub> stretching frequencies. These lower energy vibrations can be attributed to

**Table 4. Selected Bond Lengths (Å) and Angles (deg) for  $(C_5Me_5)_2YEt$ , **2****

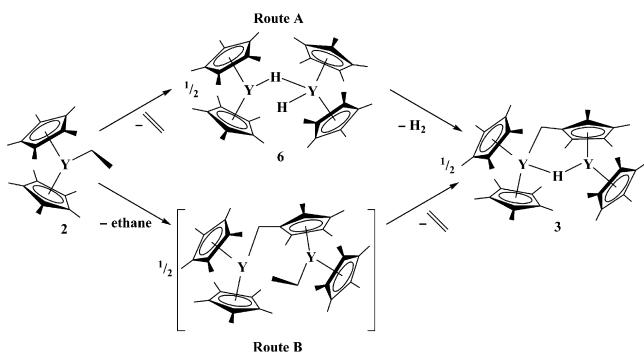
	<b>2</b>
Y–Cnt	2.350
	2.351
Y–C21	2.419(3)
Y–C22	2.682(4)
Y–H22a	2.27(3)
C21–C22	1.510(5)
Cnt–Ln–Cnt	141.5
Y–C21–C22	82.6(2)

a C–H bond that is weakened due to an agostic interaction with a metal center.<sup>39,40</sup> The IR spectrum of **2** is almost identical to that reported for  $(C_5Me_5)_2ScEt$ ,<sup>8</sup> which showed bands at 2593, 2503, and 2440  $cm^{-1}$ . The similarity in NMR and IR spectra between these two  $(C_5Me_5)_2LnEt$  complexes supports the hypothesis made by Bercau et al.<sup>8</sup> that the ethyl ligand in  $(C_5Me_5)_2ScEt$  is bent inward toward scandium, analogous to **2**.

**Decomposition.** It was expected that  $(C_5Me_5)_2YEt$ , **2**, might decompose via  $\beta$ -H elimination to form  $[(C_5Me_5)_2YH]_2$ , **6**. However, neither **6** nor ethylene was observed by <sup>1</sup>H NMR spectroscopy after allowing **2** to decompose in solution at room temperature, eq 4. The fact that one of the decomposition products,  $(C_5Me_5)_2Y(\mu-H)(\mu-\eta^1:\eta^5-CH_2C_5Me_4)Y(C_5Me_5)$ , **3**, was originally synthesized via thermal decomposition of  $[(C_5Me_5)_2YH]_2$ , **6**,<sup>50,51</sup> suggested the possibility of initial formation of **6**, followed by subsequent conversion to **3** (Scheme 1, Route A). The H<sub>2</sub> byproduct of the **6** to **3** conversion was not observed, however. The absence of H<sub>2</sub> in the NMR spectrum can be explained by the possible reaction of H<sub>2</sub> with **2** to form more transient **6** and ethane. One explanation for why ethylene is not observed is that ethylene could react with remaining **2** to form longer chained alkyl complexes, which could  $\beta$ -H eliminate to form transient **6** and the larger alkenes that were observed in the NMR spectrum. These alkenes could reinsert into unreacted **2** to give branched alkene products as well.

Another explanation for why ethane is observed in this decomposition is that **2** could be activating C–H bonds as previously shown with other  $(C_5Me_5)_2LnR$  complexes.<sup>8,9,43,45–47,56</sup> If **2** reacts with the solvent in this way, then solutions of **2** in cyclohexane-*d*<sub>12</sub> and methylcyclohexane-*d*<sub>14</sub> would produce CH<sub>3</sub>CH<sub>2</sub>D. However, no resonances for CH<sub>3</sub>CH<sub>2</sub>D were observed by <sup>1</sup>H or <sup>2</sup>H NMR spectroscopy.

**Scheme 1. Possible Pathways for the Decomposition of  $(C_5Me_5)_2YEt$ , **2**, To Form  $(C_5Me_5)_2Y(\mu-H)(\mu-\eta^1:\eta^5-CH_2C_5Me_4)Y(C_5Me_5)$ , **3**<sup>a</sup>**



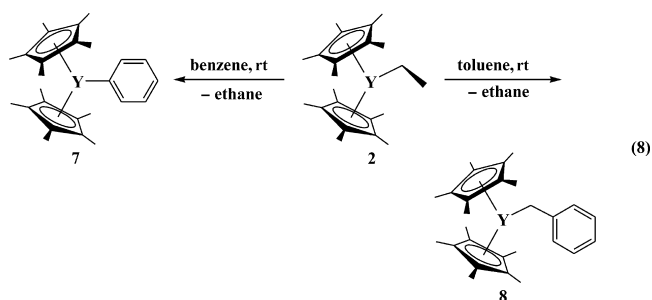
<sup>a</sup>Route A:  $\beta$ -H elimination followed by C–H bond activation of  $(C_5Me_5)^{1-}$ . Route B: C–H bond activation of  $(C_5Me_5)^{1-}$  followed by  $\beta$ -H elimination.

Since the yttrium hydride complex **6** is known to perform C–H bond activation on one of the methyl groups of another  $(C_5Me_5)^{1-}$  ligand to form **3**,<sup>50,51</sup> it is possible that **2** activates a  $(C_5Me_5)^{1-}$  methyl group on a second equivalent of **2**. This would produce ethane and a possibly short-lived yttrium tuck-over ethyl complex, “ $(C_5Me_5)_2Y(\mu-Et)[\mu-\eta^1:\eta^5-CH_2C_5Me_4]Y(C_5Me_5)$ ”, which could in turn undergo  $\beta$ -H elimination to yield **3** (Scheme 1, Route B). Again, the absence of the ethylene resonance and the observation of unidentified resonances in the alkene region of the  $^1H$  NMR spectrum can be explained by the reaction of ethylene with residual **2**. No evidence for a bimolecular decomposition pathway involving two ethyl ligands and formation of ethane and an  $Y-CH_2CH_2-Y$  analogous to that found with  $La[(\mu-Et)_2AlEt_2]_3$ <sup>32</sup> was observed.

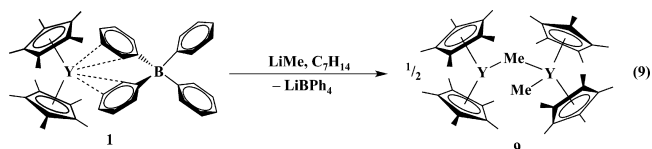
In an attempt to observe any transient species by  $^1H$  NMR spectroscopy, a solution of **2** in methylcyclohexane- $d_{14}$  was transferred to a J-Young NMR tube and allowed to decompose slowly at  $0^\circ C$  over 2 weeks, during which time the reaction was monitored periodically at  $0^\circ C$ . In this experiment, small amounts of the hydride complex **6** were identified in the  $^1H$  NMR spectrum by the pentamethylcyclopentadienyl singlet at 2.09 ppm and the signature hydride triplet at 5.45 ppm,<sup>50</sup> providing evidence that Route A may be contributing to the production of tuck-over hydride **3**. The resonances for **6** disappeared once the decomposition was complete, and ethylene and  $H_2$  were still never observed.

**Reactivity Studies. Arene Activation.** In order to evaluate the viability of Routes A and B as decomposition pathways for  $(C_5Me_5)_2YEt$ , **2**, experiments probing the reactivity of **2** were performed. To measure the ability of **2** to activate C–H bonds, several saturated and unsaturated hydrocarbons were examined. Complex **2** reacts with benzene and toluene to produce  $(C_5Me_5)_2YPh$ , **7**, and  $(C_5Me_5)_2YCH_2Ph$ , **8**, respectively, which were identified by  $^1H$  NMR spectroscopy,<sup>50</sup> eq 8. Complexes **7** and **8** were previously accessed via C–H bond activation of benzene and toluene by  $[(C_5Me_5)_2YMe]_2$ , **9**,<sup>9</sup>  $[(C_5Me_5)_2YH]_2$ , **6**,<sup>50</sup> and  $(C_5Me_5)_3Y$ .<sup>49</sup>

**Methane Activation.** Exposure of **2** to 1 atm of methane in methylcyclohexane- $d_{14}$  at room temperature in a J-Young NMR tube revealed  $^1H$  NMR resonances for the usual decomposition products (including **3**, ethane, and alkenes), but an additional broad singlet at  $-1.25$  ppm was also observed in the spectrum

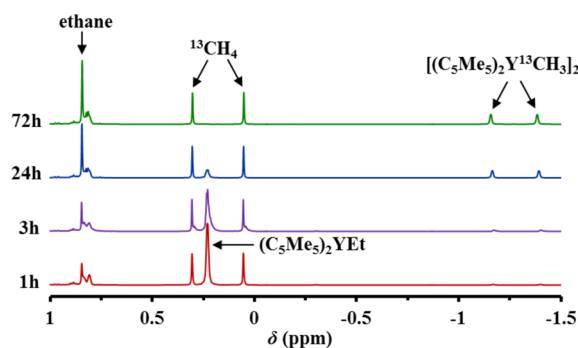


after 1 day. This is similar to the  $(Me)^{1-}$  resonance observed at  $-1.22$  ppm for  $[(C_5Me_5)_2YMe]_2$ , **9**; however, this chemical shift was recorded in cyclohexane- $d_{12}$ .<sup>9</sup> Therefore, **9** was synthesized independently, in an analogous manner to **2** and other  $[(C_5Me_5)_2LnMe]_n$  complexes<sup>46</sup> by reacting **1** with LiMe, eq 9. The yellow solid isolated from this reaction was identified



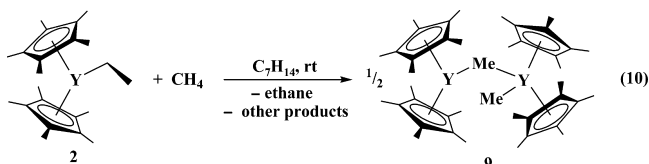
to be **9** by  $^1H$  NMR spectroscopy in cyclohexane- $d_{12}$ . Its  $^1H$  NMR spectrum in methylcyclohexane- $d_{14}$  was subsequently measured and was found to display the same methyl resonance observed at  $-1.25$  ppm in the reaction of **2** with methane, suggesting that the ethyl complex **2** is able to deprotonate  $CH_4$ . The  $C_5Me_5$  resonance of **9**, which was determined independently to appear at 1.93 ppm in methylcyclohexane- $d_{14}$  at room temperature, was not identifiable in the decomposition of **2** under methane since there were too many overlapping resonances in that region. The methyl complex **9** was estimated to be formed in about 60% yield after 72 h based on the NMR spectra.

To establish that the methyl ligand in **9** arose from **2** and methane, the decomposition of **2** in the presence of  $^{13}CH_4$  was carried out. In this isotopic labeling experiment, the singlet assigned to the methyl protons in **9** at  $-1.25$  ppm did not appear over time. Instead, a doublet ( $J = 115$  Hz) at the same chemical shift grew in concomitantly with the disappearance of the  $(C_5Me_5)^{1-}$  and  $(Et)^{1-}$  resonances of **2** and with the generation of ethane, Figure 4. This evidence supports the formation of the isotopologue,  $[(C_5Me_5)_2Y^{13}CH_3]_2$ , **9**.<sup>13</sup>C,



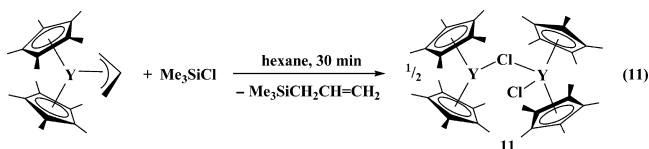
**Figure 4.**  $^1H$  NMR spectrum of the decomposition of  $(C_5Me_5)_2YEt$ , **2**, at room temperature in methylcyclohexane- $d_{14}$  under 1 atm of  $^{13}CH_4$  over 3 days. The resonances for the  $(C_5Me_5)^{1-}$  ligands and decomposition byproducts (located downfield) are not shown.

since a doublet with a large  $^1J_{\text{CH}}$  coupling constant would be expected from a  $^{13}\text{C}_3$  methyl ligand (cf.  $^1J_{\text{CH}} = 111$  Hz in  $(\text{C}_5\text{Me}_5)_2\text{ScMe}$ ,  $^8$   $^1J_{\text{CH}} \approx 108$  Hz in  $(\text{C}_5\text{Me}_5)_2\text{LuMe}$ ,  $^9$  and  $^1J_{\text{CH}} = 125$  in  $\text{CH}_4$ <sup>90</sup>). Resonances for **9**- $^{13}\text{C}$  were observed within an hour of starting the reaction. The reaction of **2** with  $\text{CD}_4$  was also examined. NMR spectroscopy supported the formation of  $[(\text{C}_5\text{Me}_5)_2\text{YCD}_3]_2$ , since a  $\text{C}_5\text{Me}_5$  resonance was observed at 1.93 ppm in the  $^1\text{H}$  NMR spectrum and a  $\text{CD}_3$  resonance was observed at  $-1.27$  ppm in the  $^2\text{H}$  NMR spectrum. Therefore, it can be concluded from the spectroscopic data that the unsolvated ethyl complex **2** is capable of activating methane, eq 10.

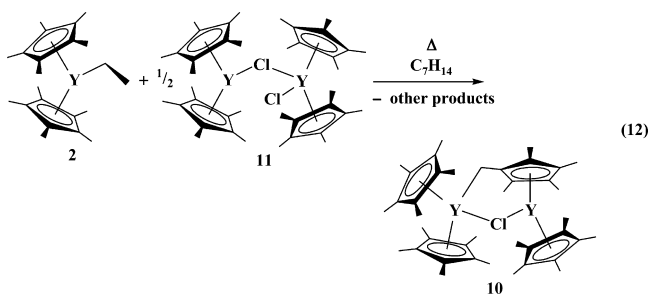


**Intermolecular Metalation of  $(\text{C}_5\text{Me}_5)^{1-}$  Ligands.** Since **2** can break a C–H bond in methane, it should be able to metalate a methyl group on a second molecule of **2** to form a tuck-over bimetallic complex proposed in Route B of Scheme 1. To determine whether this is the case, a  $(\text{C}_5\text{Me}_5)_2\text{YX}$  reagent was required such that the product of an intermolecular reaction would be stable enough to identify. Fortunately, the yttrium tuck-over chloride complex  $(\text{C}_5\text{Me}_5)_2\text{Y}(\mu\text{-Cl})(\mu\text{-}\eta^5\text{-CH}_2\text{C}_2\text{Me}_4)\text{Y}(\text{C}_5\text{Me}_5)$ , **10**, had been synthesized and fully characterized.<sup>53</sup> If **2** were to indiscriminately metalate a  $(\text{C}_5\text{Me}_5)^{1-}$  ligand in  $(\text{C}_5\text{Me}_5)_2\text{YX}$ , where X = Cl, the formation of **10** could be detected by  $^1\text{H}$  NMR spectroscopy.

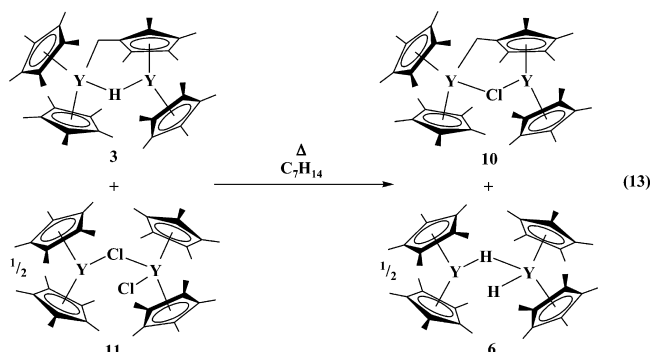
$[(\text{C}_5\text{Me}_5)_2\text{YCl}]_2$ , **11**, was previously synthesized via heating of  $(\text{C}_5\text{Me}_5)_2\text{Y}(\mu\text{-Cl})_2\text{K}(\text{THF})_2$  for 24 h under high vacuum.<sup>52</sup> However, an alternative preparation was developed where  $(\text{C}_5\text{Me}_5)_2\text{Y}(\eta^3\text{-C}_3\text{H}_5)$ , a precursor to **1**, was reacted with 1 equiv of  $\text{Me}_3\text{SiCl}$  to produce **11** in higher yield within 30 min, eq 11.



A cold solution of **2** in methylcyclohexane was added dropwise to a warm solution of excess **11** in methylcyclohexane, since the solubility of **11** is relatively low in this solvent at room temperature. In addition to the formation of typical decomposition products of **2**, the yttrium tuck-over chloride complex, **10**, was formed, as determined by  $^1\text{H}$  NMR spectroscopy,<sup>53</sup> eq 12, which is consistent with, but not

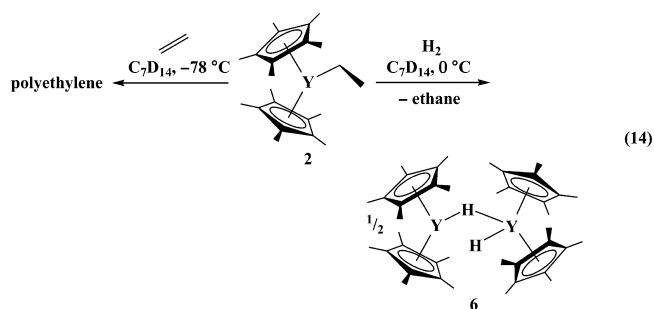


definitive for **2** metalating a  $(\text{C}_5\text{Me}_5)^{1-}$  ligand of a second metallocene complex. However, it is possible that **2** simply underwent thermal decomposition to form the tuck-over hydride, **3**, which in turn engaged in ligand exchange with **11** to produce **10** and **6**, eq 13. The hydride, **6**, would likely



convert to more **3** under these conditions. The control experiment was performed in which **3** and **11** were combined in methylcyclohexane under similar conditions. Unfortunately, the tuck-over chloride complex, **10**, was observed in this case too. This means that the formation of **10** from the reaction in eq 12 is not conclusive enough to indicate that **2** decomposes via Route B in Scheme 1.

**Reaction with  $\text{H}_2$ .** A different source of ethane could possibly be the reaction of  $\text{H}_2$  with residual **2** (Route A). This would account for the absence of  $\text{H}_2$  in the  $^1\text{H}$  NMR spectrum of the decomposition reaction of **2**. To test this, a solution of **2** in methylcyclohexane- $d_{14}$  was reacted with 1 atm of  $\text{H}_2$  at  $0^\circ\text{C}$ . Complex **6** and ethane were observed to be the major products by  $^1\text{H}$  NMR spectroscopy, eq 14.



**Ethylene Reactivity.** Regardless of whether **2** decomposes via Route A or Route B, both pathways involve  $\beta$ -H elimination as a key step. However, the absence of ethylene in the  $^1\text{H}$  NMR spectra suggests that, if formed, ethylene is likely being consumed by other species. To determine if ethylene could be inserted into the Y–Et bond of **2**, a solution of **2** in methylcyclohexane- $d_{14}$  was exposed to 1 atm of ethylene at  $-78^\circ\text{C}$ . A white insoluble material continued to form until there was a white plug in the NMR tube. The reaction was repeated on a bulk scale, and the  $^1\text{H}$  NMR spectrum and melting point of the resulting white solids were consistent with polyethylene, eq 14.

If ethylene is being produced and consumed in the decomposition of **2**, its observation would require that it be removed from the reaction such that it does not react with the remaining **2**. To accomplish this, a yellow powder of **2** was heated to  $60^\circ\text{C}$  under dynamic vacuum ( $10^{-3}$  Torr) in a Schlenk flask attached to a sealable U-tube, which was cooled to



−196 °C. After 4 h, the yellow powder became red-orange in color. The U-tube was then attached to a J-Young NMR tube containing C<sub>6</sub>D<sub>6</sub>, warmed to room temperature, and the contents were vacuum transferred into the NMR tube at −196 °C. The NMR tube was sealed and the solution was probed by <sup>1</sup>H NMR spectroscopy. The only nonsolvent resonances observed were a singlet at 5.25 ppm, corresponding to ethylene,<sup>91</sup> and a singlet at 0.80 ppm, corresponding to ethane.<sup>91</sup> The remaining red-orange powder was determined to contain a large number of unidentifiable products. This result marks a rare case in which the ethylene byproduct has been definitively detected upon decomposition of a rare earth ethyl complex, confirming that β-H elimination is indeed a key step in the decomposition of (C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>YEt, **2**.

## CONCLUSION

In summary, an extremely reactive unsolvated rare earth metallocene ethyl complex, (C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>YEt, has been synthesized, isolated, and structurally and spectroscopically characterized. The X-ray crystal structure of (C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>YEt shows an Y⋯H<sub>3</sub>C agostic interaction that is consistent with its NMR and IR spectral data. Since the spectral data on (C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>ScEt are similar, this supports the assignment of an agostic structure to the scandium complex as well. The yttrium ethyl complex is thermally unstable in solution, especially at temperatures higher than 0 °C, and can be trapped via insertion of carbodiimide and carbon dioxide into the Y–Et bond to yield stable ethylamidinate and ethylcarboxylate complexes, respectively. (C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>YEt also participates in olefin insertion, H<sub>2</sub> activation, C–H bond activation of arenes and methane, and β-H elimination processes.

## ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.5b08597.

Crystallographic data collection, structure solution, and refinement (PDF)

X-ray diffraction details of compounds **2**, **4**, and **5** (CIF)

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### Notes

The authors declare no competing financial interest.

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