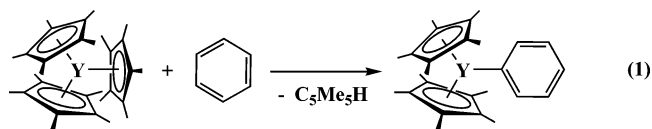


## Organolutetium Vinyl and Tuck-Over Complexes via C–H Bond Activation

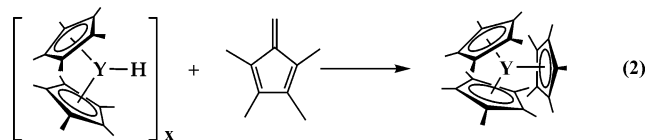
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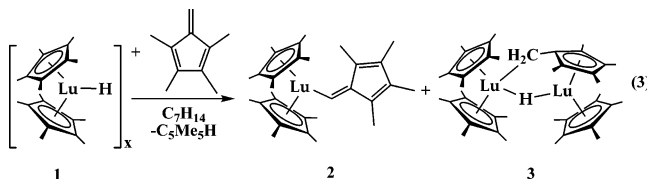
Scandium, yttrium, and lanthanide methyl and hydride metallocenes of formula  $[(C_5Me_5)_2MMe]_x$  and  $[(C_5Me_5)_2MH]_x$  are highly reactive organometallic reagents for C–H bond activation.<sup>1–12</sup> The specific reactivity is variable and depends upon the precise metal/ligand combination involved. Recent studies of the sterically crowded tris(pentamethylcyclopentadienyl) lanthanide complexes,  $(C_5Me_5)_3Ln$ ,<sup>13,14</sup> have shown that when Ln is small enough, even  $(C_5Me_5)^{1-}$  complexes can engage in C–H bond activation of arenes, eq 1.<sup>15</sup> To develop further this  $(C_5Me_5)^{1-}$ -based C–H bond



activation chemistry, the reaction of  $[(C_5Me_5)_2LuH]_x$ , **1**, with tetramethylfulvene (TMF) was examined to determine if  $(C_5Me_5)_3Lu$  would form as was observed with  $(C_5Me_5)_3Y$ , eq 2.<sup>15</sup>  $(C_5Me_5)_3Lu$  would be the most crowded of the  $(C_5Me_5)_3Ln$  lanthanide complexes and could be more reactive for C–H bond activation than  $(C_5Me_5)_3Y$ . We report here that C–H bond activation did occur, but surprisingly with the vinylic C–H bond of tetramethylfulvene.

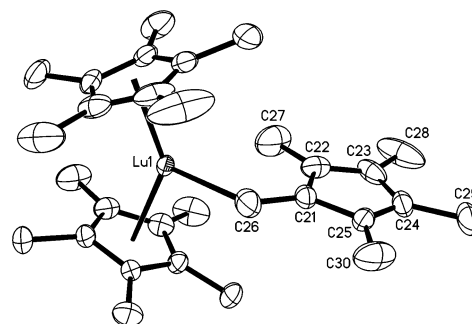


Addition of TMF to **1** in methylcyclohexane generates two metalation products,  $(C_5Me_5)_2Lu(CH=C_5Me_4)$ , **2**, a rare example of a lanthanide vinyl complex, and the “tuck-over”<sup>6,10,16</sup> complex  $(C_5Me_5)_2Lu(\mu-H)(\mu-\eta^1:\eta^5-CH_2C_5Me_4)Lu(C_5Me_5)$ , **3**, eq 3, in approximately a 2:1 ratio along with  $C_5Me_5H$ . The compounds were

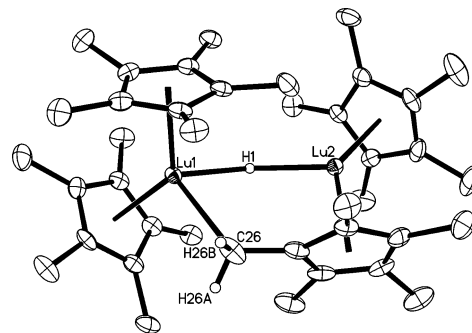


separated by crystallization and fully characterized by X-ray crystallography, Figures 1 and 2. If **1** is added slowly to a stirred solution of TMF in methylcyclohexane, then **2** can be isolated free from **3**. Complex **3** can be independently synthesized in 88% yield by heating **1** to 70 °C for 24 h.

C–H bond activation at the vinyl position in TMF instead of at an allylic methyl position was unexpected. The only other structurally characterized vinyl lanthanide in the literature is  $(Et_8\text{-calixpyrrole})(CH=CH_2)Sm(\mu^3\text{-Cl})[Li(THF)]_2[Li(THF)_2]$ .<sup>17</sup> The closest data in the literature on the activation of vinyl C–H bonds are the NMR studies of  $(C_5Me_5)_2ScMe$  with  $MeCH=CMe_2$ ,  $CH_2=CMe_2$ ,



**Figure 1.** Thermal ellipsoid plot of  $(C_5Me_5)_2Lu(CH=C_5Me_4)$ , **2**, drawn at the 40% level.



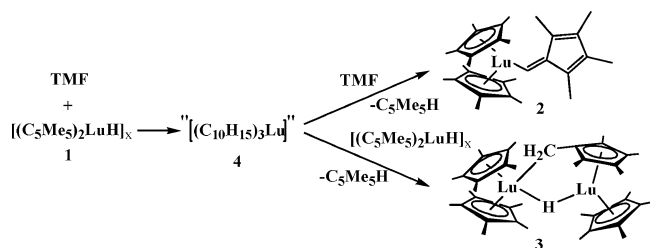
**Figure 2.** Thermal ellipsoid plot of  $(C_5Me_5)_2Lu(\mu-H)(\mu-\eta^1:\eta^5-CH_2C_5Me_4)Lu(C_5Me_5)$ , **3**, drawn at the 50% level.

$CH_2=CHMe$ , and  $CH_2=CHC_6H_4X$  ( $X = CF_3$ ,  $OMe$ ,  $Me$ ).<sup>5</sup> These NMR data also showed vinyl rather than allyl C–H bond activation. Previous studies of  $[(C_5Me_5)_2LnR]_x$  and  $[(C_5Me_5)_2LnH]_x$  have shown that specific  $\sigma$ -bond metathesis reactivity depends on a variety of factors.<sup>1–12</sup> For example, in comparison with eq 3, C–H bond activation of TMF was not observed under comparable conditions with the highly reactive  $[(C_5Me_5)_2LuMe]_x$ <sup>3,12</sup> and  $[(C_5Me_5)_2YMe]_x$ .<sup>4</sup>

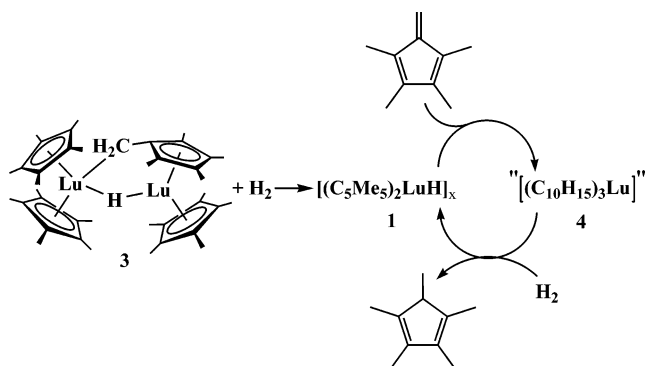
The structure of **2** contains a vinyl carbon, C(26), at a distance of 2.422(5) Å from Lu in a  $[(C_5Me_5)_2Lu]^{1+}$  metallocene unit displaying conventional metrical parameters. No Lu–C(sp<sup>2</sup>) distances are in the Cambridge Crystallographic Database for comparison, but this Lu–C length is similar to the 2.423(3) Å Lu–C (terminal-Me) distance observed in  $(C_5Me_5)_2MeLu(\mu-Me)Lu(C_5Me_5)_2$ .<sup>12</sup> The Lu–C(26) distance is surprisingly close to the 2.468–(10) Å Sm–C(CH=CH<sub>2</sub>) distance in the samarium calyx-pyrrole complex cited above<sup>17</sup> considering that Sm<sup>3+</sup> is approximately 0.1 Å larger than Lu<sup>3+</sup>.<sup>18</sup> In **2**, the methyl group involving C(27) is also oriented toward lutetium, but the 2.933(7) Å Lu–C(27) distance is quite long.

Complex **3** is similar in structure, but not isomorphous with the Ln = La<sup>16</sup>, Sm<sup>10</sup>, and Y<sup>6</sup> analogs prepared from  $[(C_5Me_5)_2LnH]_x$ . The 2.01(5) and 2.09(5) Å Lu–H distances are reasonable based on X-ray data on other lanthanide hydrides,<sup>6,10,16</sup> but as is typical with these distances, the error limits are high. The “ $(C_5Me_5)(C_5-$

Scheme 1



Scheme 2



$\text{Me}_4\text{CH}_2\text{Lu}$ ” fragment of **3** has previously been invoked as a “tuck-in” intermediate in lutetium-based C–H bond activation chemistry arising from  $[(\text{C}_5\text{Me}_5)_2\text{LuMe}]_x$ .<sup>1,3,4</sup>

The formation of the “tuck-over” complex **3** from the hydride **1** and TMF is unusual in that  $\text{C}_5\text{Me}_5\text{H}$  and not  $\text{H}_2$  is the byproduct. This suggests that **3** is formed by an undetected intermediate. This is further supported by the fact that **2** and **3** do not interconvert or react with each other and the tuckover complex **3** does not metalate TMF to make **2**. The fact that order of addition affects the product ratio suggests that **2** and **3** are formed by competitive pathways.

These observations can be rationalized by assuming that the first step in this C–H bond activation system is a reaction between **1** and TMF that is analogous to eq 2. This would make, as a transient intermediate, a tris(pentamethylcyclopentadienyl) complex of composition “ $(\text{C}_{10}\text{H}_{15})_3\text{Lu}$ ,” **4**, Scheme 1. This complex could adopt an  $(\eta^5\text{-C}_5\text{Me}_5)_3\text{Lu}$  structure like its yttrium analog,<sup>15</sup> or two possible alkyl structures  $(\eta^5\text{-C}_5\text{Me}_5)_2\text{Lu}(\eta^1\text{-C}_5\text{Me}_5)$  or  $(\eta^5\text{-C}_5\text{Me}_5)_2\text{Lu}(\text{CH}_2\text{-CHC}_4\text{Me}_4)$ , depending on the nature of the Lu–H addition. As soon as **4** is formed, it could then metalate the abundant TMF present to make **2**. Activation of the vinyl C–H bond could be explained because it is the most sterically accessible if **4** is very crowded. If the order of addition is reversed and TMF is added to **1**, the initially formed **4** could also activate a methyl C–H bond of the excess  $[(\text{C}_5\text{Me}_5)_2\text{LuH}]_x$  initially present to make the  $(\text{C}_5\text{Me}_4\text{CH}_2)^{2-}$  ion in **3**.

Scheme 1 is also consistent with the fact that the combination of **1** and TMF under hydrogen catalytically forms  $\text{C}_5\text{Me}_5\text{H}$ , Scheme 2. This catalytic hydrogenation was initiated from a mixture of **3** and TMF (which do not react) under  $\text{H}_2$ . Hydrogenolysis of the Lu–C bond in **3** generates  $[(\text{C}_5\text{Me}_5)_2\text{LuH}]_x$  which reacts with excess TMF to form **4**. Hydrogenolysis of  $(\text{C}_5\text{Me}_5)_3\text{Ln}$  complexes to form  $\text{C}_5\text{Me}_5\text{H}$  is a known reaction<sup>13–15</sup> and presumably occurs through  $(\text{C}_5\text{Me}_5)_2\text{Ln}(\eta^1\text{-C}_5\text{Me}_5)$  intermediates.

To claim the existence of a new  $(\text{C}_5\text{Me}_5)_3\text{M}$  complex, crystallographic data are generally required.<sup>13–15,19</sup> Hence, more data are desirable to support the explanation invoking “ $(\text{C}_5\text{Me}_5)_3\text{Lu}$ ” as an intermediate. However, the following experiments support the assignment of **4** as  $(\text{C}_5\text{Me}_5)_3\text{Lu}$ . In analogy to eq 1, addition of TMF to **1** in benzene and toluene generates the metalated products,  $[(\text{C}_5\text{Me}_5)_2\text{LuPh}]_x$  and  $[(\text{C}_5\text{Me}_5)_2\text{Lu}(\text{CH}_2\text{Ph})]_x$  much faster than **1** alone. Attempts to trap  $(\text{C}_5\text{Me}_5)_3\text{Lu}$  from the reaction of **1** with TMF in methylcyclohexane at  $-78^\circ\text{C}$  gave a mixture of **2** and **3** analogous to room-temperature reaction, but a new singlet in the  $^1\text{H}$  NMR spectrum was observed at  $\delta 1.97$  ppm that is close to the resonances of the other diamagnetic  $\text{La}^{22}$  and  $\text{Y}^{15}$   $(\text{C}_5\text{Me}_5)_3\text{Ln}$  complexes. The addition of TMF to this NMR sample caused the 1.97 ppm signal to disappear and the amount of **2** to increase.

In summary, these results suggest that even with the smallest lanthanide, Lu, the reactivity of  $(\text{C}_5\text{Me}_5)_3\text{Lu}$  complexes is accessible. The C–H bond activation of TMF to make **2** by this route demonstrates that new and selective C–H bond activation pathways are still accessible with the proper combination of metal and ligand. If  $(\text{C}_5\text{Me}_5)_3\text{Lu}$  is indeed the species that is catalytically hydrogenating TMF, this suggests it could be effective in selective catalytic hydrogenation of double bonds with different steric demands in a system with multiple unsaturation.

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**Supporting Information Available:** Synthetic, spectroscopic, and X-ray diffraction details (PDF, CIF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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