

# Switching from Dimerization to Cyclotrimerization Selectivity by FeCl<sub>3</sub> in the Y[N(TMS)<sub>2</sub>]<sub>3</sub>-Catalyzed Transformation of Terminal Alkynes: A New Strategy for Controlling the Selectivity of Organolanthanide-Based Catalysis

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Y[N(TMS)<sub>2</sub>]<sub>3</sub>/FeCl<sub>3</sub> has been found to be an efficient bimetallic catalyst system for the cyclotrimerization of terminal alkynes, which cannot be achieved by either trivalent iron or trivalent lanthanide catalysts. Furthermore, this reaction also occurs efficiently in the presence of Fe[N(TMS)<sub>2</sub>]<sub>3</sub> and YCl<sub>3</sub>. Both aromatic and aliphatic alkynes are compatible with this catalytic system. It is postulated that the catalytic cyclotrimerization proceeds through a tandem intermolecular diinsertion of alkynes into the yttrium–alkynyl bond and intramolecular electrophilic addition of a  $\pi$ -coordinated alkyne moiety, and the  $\pi$ -coordination of Fe<sup>3+</sup> to alkyne may play an important role in controlling the insertion degree of advancement and selectivity. The observed catalytic reaction is sharply in contrast with the cyclotrimerization of alkynes, known to proceed through a typical metallacyclopentadiene intermediate.

## Introduction

The presence of benzene ring skeletons in naturally occurring compounds and synthetic materials, coupled with the utility of aryl-based reagents in synthetic methodology, illustrates the need for efficient and versatile strategies for the construction of benzene-based structures. Metal-catalyzed cyclotrimerization of alkynes is an atom-economic method for the preparation of multisubstituted benzenes during which three new C–C bonds are formed in one step.<sup>1</sup> A great deal of work has been done in this area with

regard to mechanistic and synthetic aspects of this reaction,<sup>2</sup> and it has been successfully applied to the total synthesis of a number of natural and biologically active compounds and other interesting compounds.<sup>3</sup> A variety of metal catalysts (e.g., Co,<sup>4</sup> Ni,<sup>5</sup> Rh,<sup>6</sup> Ru,<sup>7</sup> Fe,<sup>8</sup> Pd,<sup>9</sup> Ti,<sup>10</sup> Nb,<sup>11</sup> Zr,<sup>12</sup> Ir<sup>13</sup>) have

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been used. The major limitation of these processes is that the metallic catalysts employed are often expensive and/or not easily available. Meanwhile, most of the catalysts used are limited to low-valent metal complexes or a mixture of high-valent transition metal complexes and metal reductants.<sup>4b,8b,11a,12</sup> For a long time, the use of lanthanides was disregarded within this context, mostly because they are lacking in conventional oxidative-addition/reductive-elimination processes, which are often regarded as the basis for the design of metal-catalyzed cyclotrimerizations of alkynes.

The insertion chemistry of organolanthanide complexes is an intriguing platform for catalytic design.<sup>14</sup> Significant efforts have been devoted to the development of methods for the efficient construction of complex cycles through the choice of appropriate intra- and intermolecular di- or polyinsertion reactions of organolanthanides as key steps, because of their high bond-forming efficiency, mild reaction conditions, and inherent simple experimental procedures without the production of waste.<sup>15</sup> Although organolanthanide-catalyzed reactions of terminal alkynes have been investigated extensively, only dimers and/or oligomers were obtained.<sup>16</sup> The major reason can be attributed to the similar reactivity toward the triple bond of alkynes between monoinsertion species and diinsertion ones. If a coordination insertion process is viable for a monoinsertion intermediate, it usually has a tendency for multiple insertions to further take place. As a result, less active organolanthanide catalytic systems preferentially give rise to dimers, whereas the more active ones lead to the formation of oligomers. We have

recently shown that organolanthanide complexes can undergo diinsertion reactions with isocyanates<sup>17</sup> and nitriles.<sup>18</sup> As part of a continuing effort in our laboratory toward the development of new insertions of organolanthanide compounds and their applications in organic synthesis,<sup>19</sup> we became interested in the possibility of controlling the chemo- and regioselective triinsertion of alkynes into the lanthanide–carbon bond and thus developing a new method for synthesis of trisubstituted benzenes from alkynes.

It is well known that cooperative or successive interaction of two different metals with the substrate is a useful tool for modifying the catalytic activities and selectivities and imparting to the substrate new reactions that cannot be achieved by monometallic catalyst systems.<sup>20</sup> Considering that transition metals often coordinate more strongly to alkynes than lanthanides and thus should inhibit the abstraction of enynes, we conjectured on such a synergistic scenario in controlling the insertion degree of alkynes into the lanthanide–acetylide bond and subsequent cyclization by the additional  $\pi$ -coordination of transition metal Lewis acids and hoped that such investigation of the cooperative effect of lanthanides and transition metals might lead to the development of catalyst design for cyclotrimerization of alkynes. As a preliminary testing of the concept, we herein report an unprecedented Y(III)/Fe(III) bimetallic catalyst system for cyclotrimerization of terminal alkynes, in which the Fe<sup>3+</sup> ion most probably acts as a  $\pi$ -coordinative Lewis acid. The present work demonstrates that completely different behavior in the Ln[N(TMS)<sub>2</sub>]<sub>3</sub>-catalyzed transformation of terminal alkynes can be expected depending on the presence of trivalent iron salts and opens the way toward new developments in catalytic organolanthanide chemistry.

## Results and Discussion

Readily available homoleptic bis(trimethylsilyl)amides of yttrium and lanthanide metals are currently attracting considerable attention as highly efficient catalysts for various organic transformations. In the past decade, systematic exploration of Ln[N(TMS)<sub>2</sub>]<sub>3</sub> chemistry has offered a wide range of useful methods for organic synthesis. Particular emphasis has been focused on the activation of carbon–hydrogen and heteroatom–hydrogen bonds. Successful transformations now include the Tishchenko reaction,<sup>21</sup> cross-Aldol reactions,<sup>22</sup> coupling reactions of isocyanides<sup>23</sup> and nitriles with terminal alkynes,<sup>19k</sup> dimerization of terminal alkynes,<sup>16</sup> guanylation of amines,<sup>24</sup> hydroamination,<sup>25</sup> hydrosilylation,<sup>26</sup> hydroalkoxylation<sup>27</sup> of

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**Table 1. Optimization of the Cyclotrimerization<sup>a</sup>**

| entry           | Ln (mol %) | cocatalyst (mol %)                        | T (°C) | time (h) | yield (%) <sup>b</sup> | 2a:3a <sup>c</sup> |
|-----------------|------------|---|--------|----------|------------------------|--------------------|
| 1               | Y(10)      | FeCl <sub>3</sub> (10)                    | 100    | 24       | 99                     | 98:2               |
| 2               |            | FeCl <sub>3</sub> (10)                    | 100    | 14       | 0                      |                    |
| 3               | Y(10)      | FeCl <sub>3</sub> (5)                     | 100    | 24       | 97                     | 98:2               |
| 4               | Y(10)      | FeCl <sub>3</sub> (2.5)                   | 100    | 24       | 93                     | 98:2               |
| 5               | La(10)     | FeCl <sub>3</sub> (2.5)                   | 100    | 24       | 36                     | 96:4               |
| 6               | Sm(10)     | FeCl <sub>3</sub> (2.5)                   | 100    | 24       | 66                     | 98:2               |
| 7               | Y(5)       | FeCl <sub>3</sub> (10)                    | 100    | 24       | 79                     |                    |
| 8               | Y(10)      | FeCl <sub>3</sub> (10)                    | 70     | 24       | 90                     | 98:2               |
| 9               | Y(5)       | FeCl <sub>3</sub> (5)                     | 70     | 24       | 94                     |                    |
| 10              | Y(5)       | FeCl <sub>3</sub> (5)                     | 50     | 24       | 99                     | 98:2               |
| 11              | Y(1)       | FeCl <sub>3</sub> (1)                     | 50     | 24       | 21                     |                    |
| 12              | Y(5)       | FeCl <sub>3</sub> (5)                     | 50     | 12       | 91                     |                    |
| 13 <sup>d</sup> | Y(5)       | FeCl <sub>3</sub> (5)                     | 50     | 24       | 89                     | 95:5               |
| 14 <sup>e</sup> | Y(5)       | FeCl <sub>3</sub> (5)                     | 50     | 24       | 20                     | 93:7               |
| 15              | Y(5)       | Fe(acac) <sub>3</sub> (5)                 | 50     | 24       | 58                     | 90:10              |
| 16              | Y(5)       | FeCl <sub>3</sub> (5)                     | 25     | 24       | 80                     |                    |
| 17              | Y(5)       | FeCl <sub>3</sub> (5)                     | 25     | 48       | 99                     |                    |
| 18 <sup>e</sup> | Y(5)       | InCl <sub>3</sub> (5)                     | 50     | 24       | 0                      |                    |
| 19 <sup>f</sup> | Y(5)       | ZnCl <sub>2</sub> (5)                     | 50     | 24       | 0                      |                    |
| 20 <sup>g</sup> | Y(5)       |   |        |          | 0                      |                    |
| 21              |            | Fe[N(TMS) <sub>2</sub> ] <sub>3</sub> (5) | 50     | 24       | 0                      |                    |

<sup>a</sup> Reaction conditions: 5 mL of toluene; phenylacetylene (0.2 mL, 1.82 mmol). <sup>b</sup> Isolated yield. <sup>c</sup> Determined by GC. <sup>d</sup> DCE was used as solvent. <sup>e</sup> THF was used as solvent. <sup>f</sup> Only oligomers were obtained. <sup>g</sup> Only linear dimers were obtained; see ref 16b.

unsaturated carbon–carbon bonds, and so on. Thus, with the aim of establishing whether some form of transition metal additives would govern the selectivity of organolanthanide-catalyzed reaction, we decided to use the Ln[N(TMS)<sub>2</sub>]<sub>3</sub>-catalyzed transformation of terminal alkynes as a model reaction, since it has proven to be impossible to form trisubstituted benzenes. Considering that iron salts are readily available, inexpensive, and environmentally benign,<sup>28</sup> initial investigations were carried out in the presence of various iron salts in toluene to obtain the optimum reaction conditions. The results are summarized in Table 1.

In contrast to the previously reported Y[N(TMS)<sub>2</sub>]<sub>3</sub>-catalyzed dimerization of phenylacetylene (**1a**),<sup>16b</sup> treatment of **1a** with Y[N(TMS)<sub>2</sub>]<sub>3</sub> in the presence of a catalytic amount of iron salts in toluene gave the unexpected cyclotrimerization products. Among the Lewis acids screened, FeCl<sub>3</sub> gave the best result (Table 1, entry 1). Both yield and selectivity dropped significantly when Fe(acac)<sub>3</sub> was used instead of FeCl<sub>3</sub> (Table 1, entry 15). Meanwhile, no cyclization product was obtained when InCl<sub>3</sub> and ZnCl<sub>2</sub> were used as an additive (Table 1, entries 18 and 19). Additionally, FeCl<sub>3</sub> and Fe[N(TMS)<sub>2</sub>]<sub>3</sub> by themselves were ineffective for this reaction (Table 1, entries 2 and 21).

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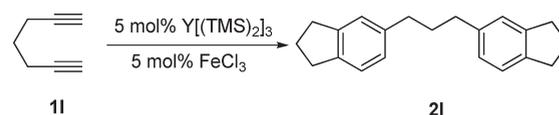
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**Table 2. Cyclotrimerization of Various Terminal Alkynes Catalyzed by Y[N(TMS)<sub>2</sub>]<sub>3</sub>/FeCl<sub>3</sub><sup>a</sup>**

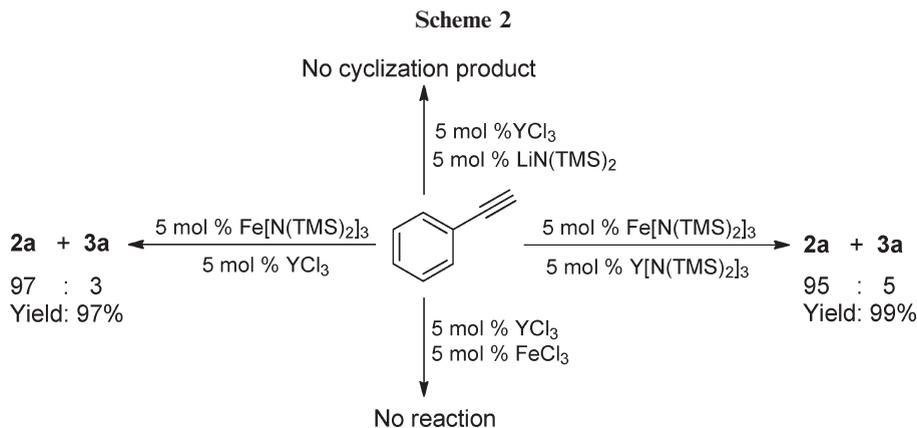
| entry | R  | isolated yield (%) | 2:3                |
|-------|--|--------------------|--------------------|
| 1     | Ph ( <b>1a</b> )   | 99                 | 98:2 <sup>c</sup>  |
| 2     | <i>p</i> -ClC <sub>6</sub> H <sub>4</sub> ( <b>1b</b> )                                | 98                 | 97:3 <sup>d</sup>  |
| 3     | <i>p</i> -F, <i>m</i> -MeC <sub>6</sub> H <sub>3</sub> ( <b>1c</b> )                   | 94                 | 99:1 <sup>c</sup>  |
| 4     | <i>p</i> -MeC <sub>6</sub> H <sub>4</sub> ( <b>1d</b> )                                | 78                 | 96:4 <sup>c</sup>  |
| 5     | <i>p</i> -(C <sub>3</sub> H <sub>11</sub> )C <sub>6</sub> H <sub>4</sub> ( <b>1e</b> ) | 80                 | 97:3 <sup>b</sup>  |
| 6     | <i>p</i> -MeOC <sub>6</sub> H <sub>4</sub> ( <b>1f</b> )                               | 74                 | 92:8 <sup>b</sup>  |
| 7     | <i>p</i> - <sup>t</sup> BuC <sub>6</sub> H <sub>4</sub> OCH <sub>2</sub> ( <b>1g</b> ) | 98                 | 88:12 <sup>b</sup> |
| 8     | <i>n</i> -butyl ( <b>1h</b> )  | 64                 | 53:47 <sup>c</sup> |
| 9     | <i>n</i> -hexyl ( <b>1i</b> )  | 60                 | 52:48 <sup>c</sup> |
| 10    | cyclohexyl ( <b>1k</b> )   | 68                 | 52:48 <sup>c</sup> |
| 11    | Me <sub>3</sub> Si ( <b>1j</b> )   | 62                 | 95:5 <sup>b</sup>  |

<sup>a</sup> Conditions: 5 mL of toluene; 50 °C; 24 h, 0.8 mmol of alkynes, 5 mol % Y[N(TMS)<sub>2</sub>]<sub>3</sub>, and 5 mol % FeCl<sub>3</sub>. <sup>b</sup> Determined by <sup>1</sup>H NMR. <sup>c</sup> Determined by GC. <sup>d</sup> Determined by HPLC.

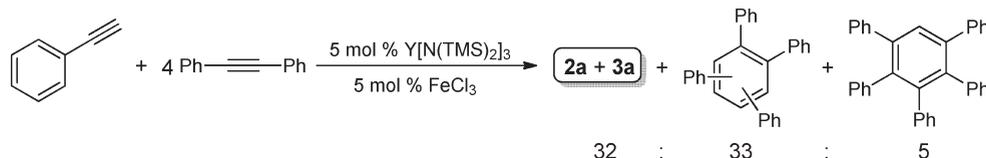
**Scheme 1. Cyclotrimerization of 1,6-Heptadiyne**

Among rare-earth metals tested, yttrium afforded the best result, giving 99% combined yield (Table 1, entries 4–6). These results demonstrate that both the lanthanide ion and the iron ion are essential, and their cooperative effects play a key role in the catalytic cyclotrimerization. Toluene was the best solvent for this reaction (Table 1, entries 10, 13, and 14). The ratio of Y[N(TMS)<sub>2</sub>]<sub>3</sub> and FeCl<sub>3</sub> was found to be important for the reaction, and the best result was achieved in the molar ratio of 1:1 (Table 1, entries 1 and 10). Notably, the cyclotrimerization reaction also proceeded quite smoothly at room temperature, although longer reaction time was required (Table 1, entry 17). When the catalysts were reduced to 1 mol %, only 21% yield was obtained (Table 1, entry 11).

Next, we explored the cyclotrimerization of various substituted terminal alkynes under optimized conditions, and the results are summarized in Table 2. The reactivity of alkynes is controlled by the steric and electronic properties of the substituents. Aromatic acetylenes with electron-withdrawing substituents, such as *p*-chlorophenylacetylene and 4-fluoro-3-(methylphenyl)acetylene, reacted smoothly to afford the corresponding 1,2,4-trisubstituted benzenes in high yield and with excellent regioselectivity (Table 2, entries 2 and 3). At the same time, electron-donating groups, like alkyls and methoxyl in the para position of benzene rings, seem to negatively affect the yield, but the regioselectivity remained essentially constant (Table 2, entries 4–6). Propargyl ether also worked well under this condition, yielding the corresponding product in almost quantitative yield with good selectivity (Table 2, entry 7). Remarkably, this heterobimetallic catalyst system also worked for aliphatic alkynes, albeit with low regioselectivities. The reaction of substrates **1h–k** afforded a nearly 1:1 mixture of **2** and **3** in moderate combined yields (Table 2, entries 8–10). The absence of regioselectivity is presumably due to steric and



**Scheme 3. Cross-Cyclotrimerization of 1a with Diphenylacetylene**



electronic reasons. Consequently, excellent regioselectivity was obtained when more sterically bulky trimethylsilylacetylene was used (Table 2, entry 11).

When 1,6-heptadiyne was used under the optimized reaction conditions, the double cyclization product (**2I**) was obtained in 72% yield with excellent chemo- and regioselectivity (Scheme 1).

Iron-mediated cyclotrimerization of alkynes has been known for a long time, but such reactions proceed through a metallacyclopentadiene intermediate. In all cases the iron must be in a low-valent oxidation state.<sup>8</sup> If trivalent iron salts are used as precatalysts, it should require the presence of a strong reductant. In any case, no cyclotrimerization product could be detected when only one of the two metals ( $\text{Fe}^{3+}$  or  $\text{Y}^{3+}$ ) was present. Furthermore, treatment of a suspension of  $\text{YCl}_3$  in toluene with  $(\text{TMS})_2\text{NLi}$  followed by reacting with excessive **1a** did not give the cyclotrimerization product too. Obviously, in the present case the cyclotrimerization is likely to operate through another mechanistic pathway involving the concerted effect between the rare-earth metal complex and the iron salt. To gain a better understanding of how the cyclotrimerization occurs under these conditions, we further examined the reaction of **1a** with  $\text{Fe[N(TMS)}_2\text{]}_3$  and  $\text{YCl}_3$ . Interestingly, the combination of  $\text{Fe[N(TMS)}_2\text{]}_3$  (5 mol %) and  $\text{YCl}_3$  (5 mol %) could also catalyze cyclotrimerization of **1a**, with a ratio of 97:3 of **2a** and **3a** in 97% total yield (Scheme 2). Moreover, the combination of  $\text{Fe[N(TMS)}_2\text{]}_3$  and  $\text{Y[N(TMS)}_2\text{]}_3$  could also catalyze cyclotrimerization of **1a**, giving the cyclization product in 99% combined yield with a ratio of **2a**:**3a** of 95:5 (Scheme 2). These results indicate that both trivalent iron and yttrium are an integral part of the whole catalytic system.

It is noteworthy that the combination of  $\text{FeCl}_3$  and  $\text{YCl}_3$  was inefficient for the catalytic cyclotrimerization of terminal alkynes. Moreover, internal alkynes such as 1-phenyl-1-propyne could not form benzene derivatives under the same conditions. These results indicate that the yttrium alkynyl might be the active species in the catalytic cyclotrimerization. In order to obtain further insight into the cyclization process, we conducted cross-cyclotrimerization of **1a** with 4 equiv of diphenylacetylene (Scheme 3). To our delight, we got the cross-cyclotrimerization

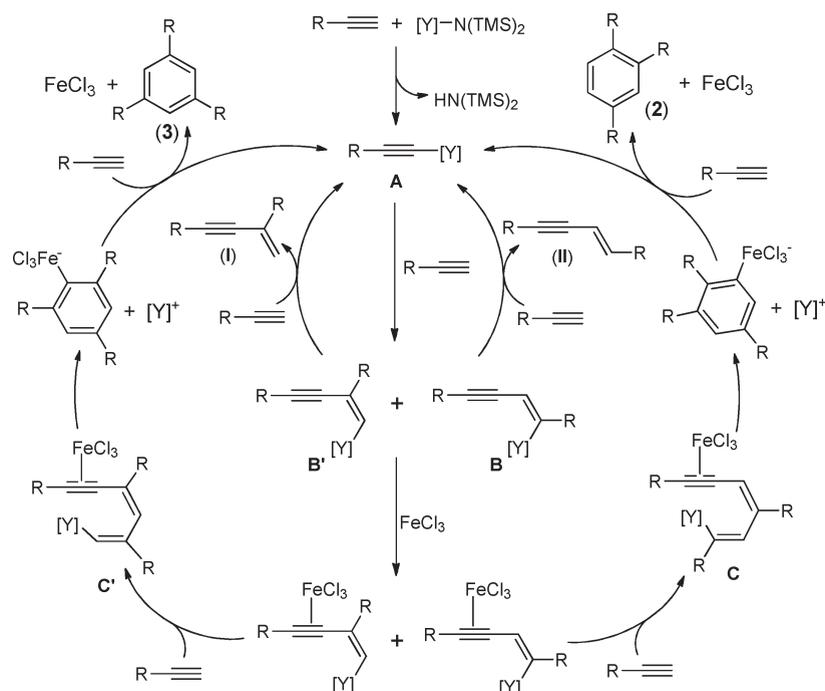
products in addition to **2a** and **3a**. However, treatment of a mixture of **1a** and **1I** with  $\text{Y[N(TMS)}_2\text{]}_3/\text{FeCl}_3$  gave only **2a** and **2I** without the isolation of the cross-cyclotrimerization product. This could be a proof for our hypothesis.

Based on the results described above, a plausible reaction pathway for  $\text{Y[N(TMS)}_2\text{]}_3/\text{FeCl}_3$  cocatalyzed cyclotrimerization of terminal alkynes is shown in Scheme 4. Terminal alkyne C–H bond activation leads to the formation of lanthanide acetylides (**A**) together with liberation of amine. Coordination and subsequent insertion of one alkyne molecule into the Ln–C bond of **A** gives key alkynyl-substituted alkenyl lanthanide intermediates (**B** and **B'**).<sup>16b</sup> A second alkyne molecule insertion of **B** and **B'** gives **C** and **C'**, respectively. Subsequently, the intramolecular nucleophilic attack of alkenyl to the Fe-coordinated alkyne moiety would lead to the formation of aryliron species.<sup>29</sup> Finally, protonation of aryl iron complexes with alkyne followed by transmetalation affords the cyclotrimerization products (**2** and **3**) and regenerates the lanthanide acetylides (**A**) and  $\text{FeCl}_3$ .

Consistent with this, the coordination of  $\text{Fe}^{3+}$  to the  $\text{C}\equiv\text{C}$  bond should play an important role in adjusting the selectivity. The presence of a coordinative iron ion should reduce the basicity of the alkynyl-substituted alkenyl ligand and thus prevent the occurrence of protonation of alkynyl-substituted alkenyl lanthanide intermediates with terminal alkynes, instead, which would be favorable to the insertion of the second alkyne molecule into the resulting yttrium–alkenyl bond. Moreover, the iron coordination also enhances the electrophilic reactivity of the related  $\text{C}\equiv\text{C}$  group and promotes the occurrence of the cyclization in the catalytic cycle. If  $\text{FeCl}_3$  is absent, the alkynyl-substituted alkenyl lanthanide complexes **B** and **B'** would undergo protonation rather than insertion of the second terminal alkyne to give the enynes **I** and **II**, as observed previously.<sup>16b</sup>

In conclusion, the yttrium(III) and iron(III)-cocatalyzed cyclotrimerization of terminal alkynes exhibits a fascinating

(29) (a) Huang, W.; Zheng, P. Z.; Zhang, Z. X.; Liu, R. T.; Chen, Z. X.; Zhou, X. G. *J. Org. Chem.* **2008**, *73*, 6845–6848. (b) Li, R. S.; Wang, S. R.; Lu, W. J. *Org. Lett.* **2007**, *9*, 2219–2222.

**Scheme 4. Proposed Mechanism for  $Y[N(TMS)_2]_3/FeCl_3$  Cocatalyzed Cyclotrimerization of Terminal Alkynes**

variation in selectivity compared to the sole organolanthanide(III)-catalyzed dimerization of terminal alkynes. To the best of our knowledge, the above-described cooperative effect in catalytic cyclotrimerization is an unprecedented phenomenon, demonstrating that the introduction of a transition metal additive into the trivalent lanthanide bis-(trimethylsilyl)amide system has a high potential to enhance catalytic activities as well as to change the catalytic selectivity, leading to the occurrence of new reactions that cannot be achieved by the corresponding monometallic catalyst systems. The present work opens the way toward new developments in catalytic organolanthanide chemistry.

### Experimental Section

**General Experimental Details.** All reactions were carried out under a nitrogen atmosphere using standard Schlenk techniques. The solvents were refluxed and distilled over sodium benzophenone ketyl under nitrogen. All substrates were commercially available and purified by standard procedures.  $^1H$  NMR and  $^{13}C$  NMR spectra were recorded on a Bruker 400 MHz using  $CDCl_3$  as solvent. GC-MS were obtained on a Hewlett-Packard 6890/5973 instrument. High-resolution mass spectra (HRMS) were recorded using ESI ionization sources.

**General Procedure for the Cyclotrimerization.** To a mixture of  $Y[N(TMS)_2]_3$  (23 mg, 0.04 mmol) and  $FeCl_3$  (6 mg, 0.04 mmol) in 5 mL of toluene was added 0.8 mmol of alkyne. The mixture was stirred at 50 °C for 24 h. Then the reaction was quenched with water, and the aqueous layer was extracted with ether ( $3 \times 10$  mL) and then ethyl acetate ( $3 \times 10$  mL). The combined organic layer was dried over  $Na_2SO_4$ . After filtration and removal of solvents under vacuum, the crude product was purified with flash chromatography using petroleum ether as eluent.

**1,2,4-Tris(4-amyllphenyl)benzene (2e).**  $^1H$  NMR ( $CDCl_3$ , 400 MHz):  $\delta$  7.64–7.57 (m, 4H), 7.47 (d,  $J = 8.4$  Hz, 1H), 7.27–7.25

(m, 3H), 7.10–7.01 (m, 7H), 2.66–2.54 (m, 6H), 1.67–1.55 (m, 6H), 1.38–1.25 (m, 12H), 0.92–0.87 (m, 9H).  $^{13}C$  NMR ( $CDCl_3$ , 100 MHz):  $\delta$  142.29, 141.21, 141.13, 141.02, 140.15, 139.37, 139.09, 138.69, 138.17, 131.13, 129.88, 129.84, 129.34, 129.01, 128.99, 128.05, 128.01, 127.07, 125.82, 35.76, 35.68, 31.73, 31.64, 31.62, 31.33, 31.15, 31.14, 22.73, 22.70, 14.22, 14.20. HRMS-ESI: calcd for  $C_{39}H_{48}$  516.3756, found 516.3758.

**1,2,4-Tris(4-*tert*-butylphenoxymethyl)benzene (2g).**  $^1H$  NMR ( $CDCl_3$ , 400 MHz):  $\delta$  7.66 (s, 1H), 7.59 (d,  $J = 7.4$  Hz, 1H), 7.49 (d,  $J = 7.4$  Hz), 7.38–7.35 (m, 6H), 6.99–6.96 (m, 6H), 5.21 (s, 4H), 5.12 (s, 2H), 1.37 (s, 27H).  $^{13}C$  NMR ( $CDCl_3$ , 100 MHz):  $\delta$  156.65, 156.56, 156.53, 143.92, 143.88, 143.83, 143.79, 138.25, 137.64, 135.78, 135.18, 129.28, 128.04, 127.40, 126.40, 114.46, 114.44, 114.43, 69.75, 68.10, 67.89, 34.22, 31.67. HRMS-ESI: calcd for  $C_{39}H_{48}O_3$  564.3603, found 564.3600.

**1,2,4-Tris(cyclohexylphenyl)benzene (2k) and 1,3,5-Tris(cyclohexylphenyl)benzene (3k).**  $^1H$  NMR ( $CDCl_3$ , 400 MHz) of the mixture of the two products:  $\delta$  7.16 (d,  $J = 8$  Hz, 1H), 7.08 (d,  $J = 2$  Hz, 1H), 7.01 (dd,  $J = 8.0, 1.6$  Hz, 1H), 6.89 (s, 3H), 2.81–2.76 (m, 2H), 2.51–2.44 (m, 4H), 1.91–1.74 (m, 24H), 1.50–1.25 (m, 36H).  $^{13}C$  NMR ( $CDCl_3$ , 100 MHz) of the mixture of the two products:  $\delta$  147.93, 145.16, 144.63, 142.19, 125.72, 124.60, 123.99, 123.05, 44.96, 44.46, 39.42, 39.15, 34.88, 34.85, 34.73, 34.65, 27.47, 27.46, 27.19, 27.18, 26.52, 26.42, 26.41. HRMS-ESI: calcd for  $C_{24}H_{36}$  324.2817, found 324.2825.

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