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Multimetallic Zirconocene-Based Catalysis: Alkyne Dimerization and Cyclotrimerization Reactions

Antoine Joosten,[†] Mohamad Soueidan,[‡] Clément Denhez,[†] Dominique Harakat,[†]
Florence Hélion,[‡] Jean-Louis Namy,[*,‡] Jean-Luc Vasse,[†] and Jan Szymoniak[*,†]

Institut de Chimie Moléculaire de Reims, CNRS (UMR 6229), Université de Reims, 51687 Reims Cedex 2, France, and Laboratoire de Catalyse Moléculaire, CNRS (UMR 8182), ICMMO, Bat 420, Université Paris-Sud, 91405 Orsay, France

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Systematic exploration of zirconocene (Cp$_2$Zr^{II}) chemistry since the 1980s has offered a wide range of useful methods for organic synthesis. Many of these reactions are stoichiometric in zirconium, and even if several catalytic reactions are known, the development of catalytic zirconocene chemistry is of continuing interest. In this paper, the study of reactions catalytic in zirconium, i.e. alkyne dimerization and cyclotrimerization, is presented. These reactions are carried out by employing the recently introduced lanthanide-originated zirconocene equivalent. The use of 10 mol % of Cp$_2$ZrCl$_2$, together with La metal or mischmetall as reductant and AlCl$_3$ as transmetalating agent, leads to an efficient formation of dienes from disubstituted alkynes. Under the same conditions, monosubstituted alkynes underwent cyclotrimerization reactions to afford benzene derivatives. This reaction also occurs efficiently in the absence of AlCl$_3$. It was postulated that the catalytic cyclotrimerization did not proceed through a typical insertion of the alkyne into the zirconacyclopentadiene intermediate. This unprecedented reaction takes place in the presence of zirconocene and lanthanide species, possibly involving a bimetallic polarization process.

Introduction

Extensive exploration of zirconocene (Cp$_2$Zr^{II}) chemistry in the last two decades[1] has been supported by the introduction of practical methods for generating low-valent zirconocene species in situ. Among them, alkene−zirconocene complexes appeared as particularly useful reagents. The so-called Negishi reagent, i.e. (1-butene)ZrCp$_2$, can be generated by treatment of Cp$_2$ZrCl$_2$ with 2 equiv of *n*-BuLi at −78 °C and warming to room temperature,[2] and it has been widely used as an efficient "Cp$_2$Zr" equivalent.[3] Similarly, (ethylene)ZrCp$_2$ can be generated by treatment of Cp$_2$ZrCl$_2$ with 2 equiv of EtMgBr.[4] In addition to a wide stoichiometric low-valent zirconocene chemistry, there are also several zirconocene-catalyzed C−C bond-forming reactions. Some of them, such as the Zr-catalyzed ethylmagnesation of alkenes,[5,6] bicyclization of dienes,[7] and the oxidative addition of allyl derivatives,[8] proceed through generation and carbometalative ring expansion (cyclic carbozirconation) of zirconacyclopropanes (alkene−zirconocenes) and zirconacyclopropenes. The carboalumination of alkynes[9] and alkenes[10,11] reveal dichotomous mechanisms involving cyclic or acyclic bimetallic carbometalation processes.[12] The extensive development of asymmetric reactions using chiral zirconocene catalysts[13] are noteworthy. Among them, the Zr-catalyzed asymmetric carboalumination of alkenes has been developed by

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* To whom correspondence should be addressed. E-mail: jan.szymoniak@univ-reims.fr (J.S.); jelonamy@icmo.u-psud.fr (J.-L.N.).

[†] Université de Reims.

[‡] Université Paris-Sud.

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Negishi[14] and widely applied to the synthesis of natural products.[15] Diene cyclization was studied and applied to the preparation of carbocycles and nitrogen heterocycles by Mori.[16] Asymmetric carbomagnesation of unactivated or functionalized alkenes was successfully developed by Hoveyda[17] and Whitby.[18] Although the reactions catalytic in zirconium have been extensively studied, a number of Zr-mediated reactions remain stoichiometric and the development of new catalytic processes is important.

We recently reported a room-temperature-based protocol for the generation of an alkene-free zirconocene equivalent, by reducing Cp_2ZrCl_2 with readily available mischmetall (an alloy of Ce, La, Nd, and Pr).[19] Ce and La (but not Nd) metal components of mischmetall have been demonstrated to act efficiently as reductants.[19] By using this reagent, not only reactions typical for zirconocene were carried out but also some others: i.e., coupling of terminal alkynes as well as intermolecular coupling of alkynes with imines. The mild and direct method applied for the generation of a lanthanide-originated Cp_2Zr equivalent offers the possibility of developing new reactions catalytic in zirconium.[20] The model experiments for such studies could involve alkyne−alkyne couplings, which are known to proceed through zirconacyclopentadienes under stoichiometric conditions.[21] These dimerization reactions easily occur in the presence of a stoichiometric amount of zirconocene. The present work demonstrates the feasibility of such couplings by using catalytic amounts of Cp_2ZrCl_2 and opens the way toward new developments in catalytic organozirconium chemistry.

Results and Discussion

By using the lanthanide-originated Cp_2Zr equivalent, zirconacyclopentadiene complexes have already been demonstrated to form from both internal and terminal alkynes.[19] Furthermore, zirconacyclopentadienes are known to undergo transmetalations, especially to copper and nickel, which can be followed by insertions or other reactions, leading to diversely functionalized organic compounds.[21] We envisioned that the alkyne coupling might be carried out by using a catalytic amount of Cp_2ZrCl_2, together with a lanthanide reductant and CuCl (2 equiv) or $NiX_2(PPh_3)_2$ (1 equiv) (X = Cl, Br), which have been typically used as transmetalating agents. In such cases, the initially formed zirconacyclopentadiene would be transmetalated to give a metallacycle (Ni) or a bimetallic (Cu) intermediate (**A**), thus generating Cp_2ZrCl_2, which in turn would be reduced to close the catalytic cycle (Scheme 1).

Scheme 1

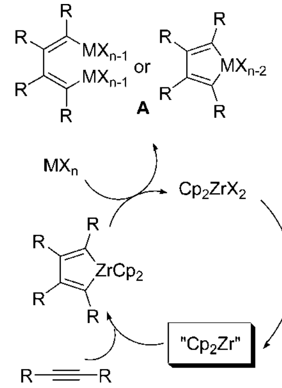
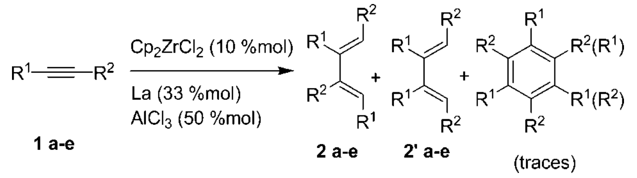


Table 1. Catalytic Dimerization of Disubstituted Alkynes



entry	R^1	R^2	time (h)	product (yield (%))[a]
1	*n*-Pr	*n*-Pr	7	**2a** (76)
2	Me	Ph	8	**2b**[b] (75)
3	Ph	Ph	48	**2c** (31)
4	*n*-Pr	Ph	12	**2d**[b] (85)
5	Me	Me_3Si	1.5	**2′e** (65)

[a] Isolated yields. [b] Topoisomers (10%).

However, when Cu and Ni salts were used, no catalytic dimerization was observed, and only complex reaction mixtures were systematically obtained.[22] Although transmetalation of zirconocene complexes to aluminum is well-known, only a few examples involving zirconacyclopentadienes have been reported.[23] In these reactions, aluminacyclopentadienes have been postulated to form only under specific conditions (in the presence of an aldehyde−$AlCl_3$ adduct). Despite these limitations, in the next experiments $AlCl_3$ was employed. The mixture of a catalytic amount of Cp_2ZrCl_2 (10 mol %) together with powdered La metal (33 mol %) and $AlCl_3$ (50 mol %) was stirred until the color turned deep red (about 10 min).[24] Oct-4-yne (**1a**) was then added, and the reaction mixture was warmed at 50 °C. A total conversion of **1a** was observed by GC-MS after 7 h, and (4*E*,6*E*)-5,6-dipropyldeca-4,6-diene (**2a**) was obtained after a hydrolytic workup in 76% yield, accompanied by only a small amount (about 5%) of hexapropylbenzene (Table 1). Moreover, the total deuterium incorporation at each terminal position of the diene **2a** upon deuterolysis confirms the formation of the metalacyclopentadiene intermediate. The decrease in the amount of Cp_2ZrCl_2 to 5 mol % made the reaction time longer (12 h) and slightly lowered the yield (69%). In the absence of $AlCl_3$, the partial conversion of **1a** to **2a** corresponded to the amount of Cp_2ZrCl_2 used. The decrease

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(24) A change of color from yellow to red indicates the formation of Cp_2Zr^{II} species.[19]

in $AlCl_3$ up to 5 mol % resulted in the conversion of **1a** to **2a** in the range of 20−30%, relative to the combined amounts of Cp_2ZrCl_2 and $AlCl_3$ involved in the reaction. These results were in accordance with a noticeable transmetalation process, to ensure the coupling of **1a** catalytic in zirconium, as anticipated in Scheme 1. The successful transmetalation of the intermediate zirconacyclopentadiene with $AlCl_3$ is noteworthy. It might involve the $AlCl_3$ reactivity tuning through chlorine-bridged $Cl_2LaCl-AlCl_3$ species, similarly to the reactions in which an aldehyde−$AlCl_3$ adduct was involved.[23]

By applying a catalytic amount of Cp_2ZrCl_2 together with stoichiometric amounts of the La metal and $AlCl_3$, other disubstituted alkynes (**1b**−**e**) similarly reacted to afford the corresponding tetrasubstituted dienes (**2b**−**e**) (Table 1). They were accompanied by a small amount (≤5%) of the corresponding hexasubstituted benzene derivatives.

As for **1a**, methylphenylacetylene (**1b**) was converted into the diene **2b** in the same good yield (entry 2). In contrast, the total consumption of diphenylacetylene (**1c**) was obtained only after a 48 h period, and the diene **2c** was isolated in 31% yield (entry 3).[25] However, when using phenylpropylacetylene, a very good yield was obtained (entry 4). In this case, the dissymmetric isomer **2d** was the major product formed (85% yield); it was accompanied by two other topoisomers: i.e., (2*E*,4*E*)-3,4-diphenylhexa-2,4-diene and (1*E*,3*E*)-2,3-dimethyl-1,4-diphenylbuta-1,3-diene (10% combined yield). This marked toposelectivity is presumably due to steric reasons. The use of the silylated alkyne **1e** led to a rapid and totally toposelective dimerization reaction to afford solely the diene **2′e**, having trimethylsilyl groups at the terminal C atoms (entry 5). Trimethylsilyl−alkyne couplings are known to give selectively α-silylated zirconacyclopentadiene intermediates.[26] Similar results were obtained by using mischmetall instead of La as reductant. Thus, dimerization of disubstituted alkynes proved to occur when using a catalytic amount of lanthanide-originated zirconocene and $AlCl_3$ as additive. A generally slow dimerization of disubstituted dienes indicates that the Zr(II) species can regenerate over a long reaction period to allow the closing of the catalytic cycle. As anticipated in Scheme 1, and similarly to some Zr-catalyzed reactions (see Introduction), the dimerization would involve carbometalative ring expansion of the zirconacyclopropene and transmetalation.

As mentioned previously, when the lanthanide-originated Cp_2Zr equivalent is applied, stoichiometric coupling of not only internal but also terminal alkynes can be carried out.[19] Therefore, we decided to check if terminal alkynes can undergo such reactions *also in the presence of a catalytic amount of zirconium*. In the model series of experiments, phenylacetylene (**3**) was used as the starting material. The experimental conditions were similar to those employed for disubstituted alkenes, involving a catalytic amount (5 mol %) of Cp_2ZrCl_2 and stoichiometric amounts of La and $AlCl_3$. The reaction was carried out in THF at 50 °C and monitored by GC-MS. Alkyne **3** was completely consumed after 2 h and, surprisingly, a mixture of 1,2,4- and 1,3,5-triphenylbenzene (**4a**,**b** respectively, **4a**:**4b** = 3:2) was mainly formed, accompanied by only a small amount of the expected diphenylbutadiene **5** (1,3- and 1,4-isomers) (Scheme 2).

Scheme 2

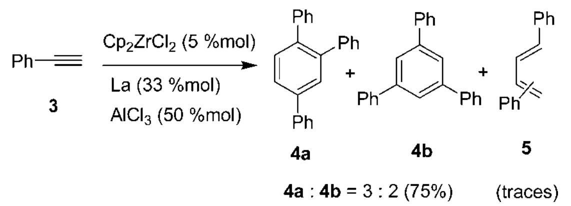
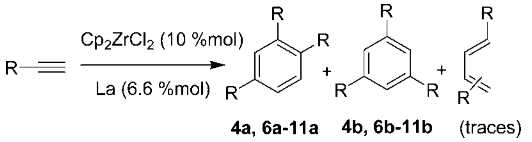


Table 2. Cyclotrimerization of Terminal Alkynes



entry	R	time (h)	isomer ratio (**a**:**b**)	product (yield (%))[a]
1	Ph	2	1.5	**4** (75)
2	4-MeC_6H_4	2	1.1	**6** (80)
3	4-$MeOC_6H_4$	2	1.1	**7** (71)
4	1-naphthyl	12		**8** (80)
5	4-biphenyl	2		**9** (80)
6	*n*-$C_{10}H_{21}$	2	1.4	**10** (73)
7	cyclohex-1-enyl	6	7.1	**11** (67)

[a] Isolated yields.

Metal-catalyzed cyclotrimerization of alkynes (or alkynes and nitriles) to produce substituted benzenes (or pyridines) have been studied extensively.[27] Activated metals, as well as transition-metal (Co, Rh, Ni, etc.) complexes have been used, but the number of practically useful catalysts is rather limited. The observed catalytic reaction sharply contrasts with the reported zirconocene-mediated cyclotrimerizations, known to proceed under stoichiometric conditions in the presence of Cu, Ni, and Cr transmetalating agents.[21,28] We noticed that compound **4** was not formed in the presence of CuCl or $NiBr_2(PPh_3)_2$ (typically used as additives in the stoichiometric reactions), even after a prolonged (12 h) reaction period.[22]

Interestingly, the cyclotrimerization reaction was noticed to occur similarly *in the absence of $AlCl_3$*. As noted previously, the benzene derivative **4** was formed in good yield from **3**. It was also accompanied by a small amount of the diene **5**, corresponding to that of the zirconacyclopentadiene involved in the reaction.

Other monosubstituted alkynes also reacted to afford the corresponding trisubstituted benzene derivatives (Table 2). Thus, alkynes bearing aryl (entries 1−5) and alkyl (entry 6) as well as alkenyl (entry 7) groups afforded mixtures of 1,2,4- and 1,3,5-trisubstituted benzene derivatives (**4** and **6**−**11**) in typically a ratio of 1.1−1.5 (except in entry 7) and in good yields. In all cases, only traces of the corresponding dienes were detected. Similar results were obtained by using mischmetall instead of La as reductant.

The selective preparation of benzene derivatives from different alkynes is of substantial synthetic interest,[29] and in this context the coupling reaction from the diyne **12** and phenylacetylene **3** was next investigated. By applying the previously established procedure, cyclic carbozirconation was first exam-

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(25) A significant quantity of the reduction products, i.e. *trans*- and *cis*-stilbene, was formed. Compound **2c** was obtained in 86% yield after 4 h when using a stoichiometric amount of Cp_2ZrCl_2; see also ref 6.

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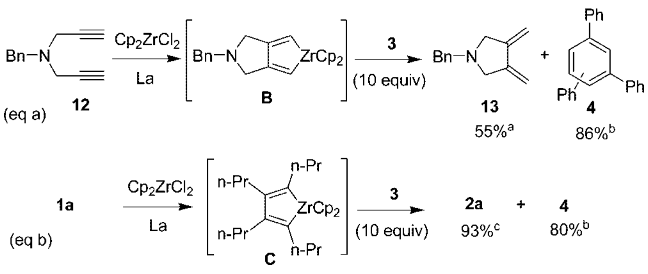
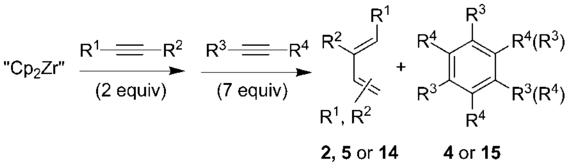
Scheme 3



^{a} Yield related to **12**.
^{b} Yield related to **3**.
^{c} Yield related to **1a**.

Table 3. Selective Formation of Dienes and Benzene Derivatives



entry	R^{1}	R^{2}	R^{3}	R^{4}	product (yield (%))^{a}
1	Ph	Ph	Ph	H	**2c** (87^{b}), **4** (75^{c})
2	Ph	H	4-$Me_2NC_6H_4$	H	**5** (81^{b}), **15** (90^{c})
3	*n*-C_5H_{11}	H	Ph	H	**14** (80^{b}), **4** (78^{c})
4	Ph	H	Ph	D	**5** (82^{b}), **4-d_3** (87^{c})
5	Ph	D	Ph	H	**5-d_2** (81^{b}), **4** (86^{c})

^{a} Isolated yields. ^{b} Yield related to $R^1C{\equiv}CR^2$. ^{c} Yield related to $R^3C{\equiv}CR^4$.

ined. The reaction mixture was analyzed by ESI-MS,[30] clearly indicating formation of the zirconacyclopentadiene intermediate **B** (Scheme 3).

Ten equivalents of **3** was added, and the reaction was carried out as previously detailed. Surprisingly, no benzene derivative which would result from the insertion of **3** into **B** was detected. The only products formed were the diene **13**[31] and the benzene derivative **4** (**4a**:**4b** ratio 3:2) (Scheme 3, eq a).

Following this intriguing result, we performed a reaction in which the zirconacyclopentadiene **C** was first generated from **1a**, followed by the addition of **3**. Similarly, no insertion product was observed. The reaction solely afforded the diene **2a** and the benzene derivative **4** (eq b). In the next reactions a catalytic amount of the first alkyne (and of Cp_2ZrCl_2) was used (Table 3). Also in these cases, only mixtures of dienes **2** and **5** (or **14**) (related to the first alkyne and the corresponding zirconacyclopentadiene) and benzene derivatives **4** (or **15**) (related to the second alkyne) were obtained. Examples are given in which terminal alkynes with aryl and alkyl groups were employed. Among them, the use of phenylacetylene **3** followed by the addition of (4-(dimethylamino)phenyl)acetylene (4-ethynyl-*N,N*-dimethylaniline) led to the exclusive formation of diphenylbutadiene **5** (1,3- and 1,4-isomer mixture) and the tris((dimethylamino)phenyl)benzene derivative **15** (entry 2). The same reaction pattern, i.e. the separate formation of the diene **14** and the benzene derivative **4**, was observed with alkynes bearing alkyl (C_5H_{11}) and aryl (phenyl) groups (entry 3). Similarly, compounds **5** and **4-d_3** or **5-d_2** and **4** were formed from phenylacetylene and its deuterated analogue (entries 4 and 5).

Some additional experiments were performed to gain an insight into the reaction. When the Negishi zirconocene equivalent was generated from Cp_2ZrCl_2 with 2 equiv of *n*-BuLi in the presence of **1c**, followed by the addition of **3** and $LaCl_3$, the cyclotrimerization was not observed: only diene **5** was formed in 73% yield after hydrolysis. The same result was obtained when the "Cp_2Zr" equivalent was generated by reducing Cp_2ZrCl_2 with Mg. Moreover, no cyclotrimerization took place when generating $LaCl_3$ from tetrachloroethane and La[32] or by using $LaCl_3$ alone or as a mixture with La.

Transition-metal-mediated cyclotrimerization reactions have been postulated to proceed through the insertion (or the concerted cycloaddition) of an alkyne to the metallacyclopentadiene.[27] However, in our case, the cyclotrimerization is likely to operate through another mechanistic pathway involving both zirconium and lanthanide species. Although catalytic couplings of alkynes under the effect of lanthanide complexes (Ln = Y, La, Ce) are known,[33] such reactions proceeding through lanthanide acetylides produce oligomeric (dimeric) rather than benzene derivatives. In any case, no cyclotrimerization product was formed when only one of two metals (Zr or La) was present. The crucial point lies in the absence of benzene derivatives incorporating both alkynes, when preforming the zirconacyclopentadiene from the first alkyne and subsequently adding a different second alkyne (Scheme 3 and Table 3). If the cyclotrimerization product had formed through insertion of the alkyne into the zirconacyclopentadiene intermediate, a mixed benzene derivative would have been obtained, in addition to that formed from the second alkyne. Particularly relevant examples are those in which very similar alkynes, i.e. phenylacetylene and its deuterated analogue, were used (Table 3, entries 4 and 5), leading to the separate formation of the corresponding diene and benzene derivatives. Consequently, the cyclotrimerization reactions involving a unique alkyne, as depicted in Scheme 2 and Table 2, would not proceed through an insertion of the alkyne into the zirconacyclopentadiene intermediate.

The described cyclotrimerization appears to take place under specific conditions, in the presence of zirconocene and lanthanide components. The exact structure of the zirconocene equivalent formed from Cp_2ZrCl_2 and La as well as that of the hypothetical cyclotrimerization active (bimetallic?) species remains unknown. However, the initially formed zirconacycle appear to be invariably present in the reaction medium, in stoichiometric or catalytic amount, together with the La species, to promote the cyclotrimerization reaction. The lanthanide entity seems to be different from $LaCl_3$ that would be initially formed from Cp_2ZrCl_2 and La (according to simple stoichiometry), since no cyclotrimerization reaction takes place when adding $LaCl_3$ to the Negishi zirconocene equivalent. Possibly, a bimetallic polarization process through zirconocene–lanthanide chlorine-bridged assemblies is involved. More detailed mechanistic studies are needed to provide further insight into this unusual cyclotrimerization reaction.

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(29) No high-yielding and selective general approach to alkyne cyclotrimerization has been developed to date.

(30) For a recent review on the uses of electrospray ionization mass spectrometry for studying intermediates and reaction mechanisms, see: (a) Santos, L. S. *Eur. J. Org. Chem.* **2008**, 235. (b) For experimental and calculated HRMS spectra of **B**, see the Supporting Information.

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In conclusion, we have reported a new reactivity pattern of a lanthanide-derived zirconocene equivalent. Reactions catalytic in zirconium, i.e. alkyne dimerization and unusual cyclotrimerization in the presence of Zr and La species, have been described. Further studies of these and other similar reactions should contribute to the development of catalytic zirconocene chemistry.

Experimental Section

All reactions were conducted under an atmosphere of argon using standard Schlenk techniques. Prior to use, tetrahydrofuran was distilled under argon from sodium benzophenone ketyl. Zirconocene dichloride was purchased from Strem Chemicals. Alkynes were purchased from Aldrich and used as received. Lanthanum and mischmetall ingots were purchased from Aldrich and Fluka, respectively, and powdered using a rap under argon. ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$, unless specified, on a Bruker AC-360 spectrometer. Chemical shifts are reported in delta (δ) units, expressed in parts per million (ppm). NMR characteristics of all known compounds were in accordance with the literature data.[19,31,34–40]

Electrospray Ionization Mass Spectrometry (ESI-MS). All experiments (MS and HRMS) were performed by using a hybrid tandem quadrupole/time-of-flight (Q-TOF) instrument, equipped with a pneumatically assisted electrospray (Z-spray) ion source (Micromass, Manchester, U.K.) operated in positive mode (EV = 30 V, 80 °C, flow of injection 5 μL/min).

General Procedure for the Preparation of Dienes. A Schlenk tube was loaded with Cp_2ZrCl_2 (60 mg, 0.2 mmol), lanthanum or mischmetall (0.66 mmol), $AlCl_3$ (134 mg, 1 mmol), and THF (5 mL) under an atmosphere of argon. The resulting mixture was stirred vigorously at 50 °C until a deep red color appeared. At this stage, the alkyne (2 mmol) was added to the reaction mixture and the stirring was continued at 50 °C for 2−48 h. An aqueous HCl solution (0.1 M, 5 mL) was then added at room temperature. The aqueous layer was extracted with CH_2Cl_2 (2 × 5 mL), and the organic phases were combined, dried over $MgSO_4$, and concentrated under vacuum. The residue was purified by flash column chromatography on silica gel using a mixture of hexane and AcOEt as eluant to give the diene.

(4*E*,6*E*)-5,6-Dipropyldeca-4,6-diene (2a).[19] Oct-4-yne (146 μL, 1 mmol) was used. Yellow oil. Yield: 76%. ^{1}H NMR: δ 5.37−5.33 (t, J = 7.2 Hz, 2H), 2.16−2.02 (m, 8 H), 1.43−1.30 (m, 8 H), 0.93−0.85 (m, 12 H). ^{13}C NMR: δ 141.2 (2 C), 125.9 (2 CH), 30.3 (2 CH_2), 30.0 (2 CH_2), 23.2 (2 CH_2), 22.0 (2 CH_2), 14.1 (2 CH_3), 13.9 (2 CH_3). MS (IE, 70 eV): m/z 222 (88, M), 179 (100), 137 (45), 123 (42), 94 (48), 81(36), 55 (21).

(1*E*,3*Z*)-1,3-Diphenyl-2-methylpenta-1,3-diene (2b).[34] 1-Phenylprop-1-yne (125 μL, 1 mmol) was used. White oil, Yield: 75%. ^{1}H NMR: δ 7.48−7.15 (m, 10 H), 6.15 (s, 1 H), 6.13−6.01 (q, J = 6.9 Hz, 1H), 2.12 (s, 3 H), 1.66−1.63 (d, J = 6.9 Hz, 3 H). ^{13}C NMR: δ 145.6 (C), 139.8 (C), 138.7 (C), 138.6 (C), 129.9 (2 CH), 129.4 (CH), 129.2 (2 CH), 128.0 (2 CH), 127.7 (2 CH), 126.5 (CH), 126.1 (CH), 123.2 (CH), 15.7 (CH_3), 15.5 (CH_3). MS (IE, 70 eV): m/z 234 (M, 45), 219 (100), 204 (47), 115 (20), 91 (13).

(1*E*,3*E*)-1,2,3,4-Tetraphenylbutadiene (2c).[35] 1,2-Diphenylethyne (180 μL, 1 mmol) was used. White solid. Mp: 182 °C. Yield: 75%. ^{1}H NMR: δ 6.46 (s, 2 H), 6.81−7.92 (m, 20 H). ^{13}C NMR: δ 145.6 (2 C), 139.7 (2 C), 137.2 (2 C), 131.6 (2 CH), 130.4 (4 CH), 129.5 (4 CH), 128.8 (4 CH), 127.8 (4 CH), 127.3 (2 CH), 126.6 (2 CH).

(1*E*,3*Z*)-1,3-Diphenyl-2-propylhepta-1,3-diene (2d). Pent-1-ynylbenzene (160 μL, 1 mmol) was used. Pale yellow oil. Yield: 85%. ^{1}H NMR: δ 7.32−7.21 (m, 10 H), 6.25 (s, 1 H), 5.96−5.90 (t, J = 7.3 Hz, 1 H), 2.46−2.40 (m, 2 H), 2.06−1.98 (q, J = 7.6 Hz, 2 H), 1.64−1.43 (m, 4 H), 1.01−0.90 (m, 6 H). ^{13}C NMR: δ 144.8 (C), 143.4 (C), 140.1 (C), 138.6 (C), 129.7 (2 CH), 129.1 (CH), 128.7 (2 CH), 128.1 (CH), 128.0 (2 CH), 127.9 (2 CH), 126.5 (CH), 126.1 (CH), 31.6 (CH_2), 30.5 (CH_2), 23.1 (CH_2), 22.5 (CH_2), 14.2 (CH_3), 13.8 (CH_3). MS (IE, 70 eV): m/z 290 (M, 9), 247 (57), 205 (100), 91 (28).

(1*E*,3*E*)-2,3-Dimethyl-1,4-bis(trimethylsilanyl)buta-1,3-diene (2′e).[34] Ethynyltrimethylsilane (148 μL, 1 mmol) was used. Colorless oil. Yield: 62%. ^{1}H NMR: δ 5.70 (s, 2 H), 2.00 (s, 6 H), 0.16 (s, 18 H). ^{13}C NMR: δ 153.6 (2 C), 126.0 (2 CH), 19.8 (2 CH_3), 0.1 (6 CH_3). MS (IE, 70 eV): m/z 226 (19, M), 211 (20), 152 (20), 123 (77), 73 (100).

General Procedure for the Preparation of Trisubstituted Benzenes. A Schlenk tube was loaded with Cp_2ZrCl_2 (292 mg, 1 mmol), lanthanum or mischmetall (0.66 mmol), and THF (3 mL) under an atmosphere of argon. The resulting mixture was vigorously stirred at 50 °C until a deep red color appeared. At this stage, the alkyne (10 mmol) was added to the reaction mixture, and the stirring was continued for 2−48 h at 50 °C. The reaction was then quenched with an aqueous HCl solution (0.1 M, 5 mL). The aqueous layer was extracted with CH_2Cl_2 (2 × 5 mL), and the organic phases were combined, dried over $MgSO_4$, and concentrated under vacuum. The residue was purified by flash column chromatography on silica gel using a mixture of hexane and AcOEt as eluant to give the corresponding trisubstituted benzene.

Triphenylbenzene (4). Phenylacetylene (1.10 mL) was used. White solid. Yield: 75%. ^{1}H NMR: 1,3,5-isomer, δ 7.85 (s, 3 H), 7.71−7.23 (m, 15 H); 1,2,4-isomer, δ 7.23−7.71 (m, 18 H). ^{13}C NMR: 1,3,5-isomer, δ 142.4 (3 C), 141.1 (3 C), 128.3 (6 CH), 127.5 (3 CH), 127.4 (6 CH), 125.3 (3 CH); 1,2,4-isomer δ 142.2 (C), 141.7 (C), 141.2 (C), 140.5 (C), 140.3 (C), 139.5 (C), 130.5 (CH), 130.3 (2 CH), 129.2 (2 CH), 129.1 (CH), 129.0 (2 CH), 128.2 (2 CH), 127.4 (2 CH), 127.3 (CH), 127.2 (2 CH), 127.1 (CH), 126.7 (CH), 125.8 (CH). HRMS (EI, 70 eV): m/z $[M]^+$ calcd for $C_{24}H_{18}$ 306.1403, found 306.1401.

Tris(4-methylphenyl)benzene (6).[36] 1-Ethynyl-4-methylbenzene (1.26 mL) was used. White solid. Yield: 75%. ^{1}H NMR: 1,3,5-isomer, δ 7.82 (s, 3 H), 7.12−7.38 (m, 12 H), 2.48 (s, 9 H); 1,2,4-isomer, δ 7.12−7.38 (m, 15 H), 2.39 (s, 3 H), 2.41 (s, 3 H), 2.47 (s, 3 H). ^{13}C NMR: 1,3,5-isomer, δ 142.1 (3 C), 138.4 (3 C), 137.2 (3 C), 129.5 (6 CH), 127.2 (6 CH), 124.5 (3 CH), 21.2 (3 CH_3); 1,2,4-isomer, δ 141.4 (C), 140.7 (C), 140.0 (C), 139.1 (C), 138.7 (C), 138.3 (C), 137.7 (C), 136.1 (C), 135.9 (C), 130.4 (CH), 130.3 (2 CH), 129.8 (2 CH), 129.8 (2 CH), 129.62 (2 CH), 129.6 (2 CH), 127.6 (CH), 126.9 (2 CH), 125.2 (CH), 21.2 (CH_3), 21.1 (CH_3), 21.0 (CH_3). HRMS (EI, 70 eV): m/z $[M]^+$ calcd for $C_{27}H_{24}$ 348.1873, found 348.1867.

Tris(4-methoxyphenyl)benzene (7).[36] 1-Ethynyl-4-methoxybenzene (1.26 mL) was used. White solid. Yield: 71%. ^{1}H NMR: 1,3,5-isomer:, δ 7.80 (s, 3 H), 6.78−7.36 (m, 12 H), 3.88 (s, 9 H); 1,2,4-isomer: δ 7.36−6.78 (m, 15 H), 3.88 (s, 3 H), 3.87 (s, 3 H), 3.80 (s, 3 H). ^{13}C NMR: 1,3,5-isomer, δ 159.3 (3 C), 142.6 (3 C), 134.1 (3 C), 129.9 (3 CH), 123.8 (6 CH), 114.2 (6 CH), 55.3 (3 CH_3); 1,2,4-isomer δ 159.2 (C), 158.3 (C), 158.2 (C), 140.4 (C),

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139.6 (C), 138.4 (C), 133.9 (C), 133.8 (C), 133.2 (C), 131.0 (CH), 130.8 (2 CH), 128.8 (CH), 128.1 (2 CH), 125.3 (CH), 123.8 (2 CH), 114.4 (2 CH), 113.4 (2 CH), 113.3 (2 CH), 55.30 (CH_3), 55.29 (CH_3), 55.1 (CH_3). HRMS (EI, 70 eV): *m/z* $[M - CH_3]^+$ calcd for $C_{26}H_{21}O_3$ 381.1485, found 381.1485.

Tris(1-naphthyl)benzene (8).[37] 1-Ethynyl-1-naphthalene (1.42 mL) was used. White solid. Yield: 80%. ^{1}H NMR: δ 1,3,5-isomer 8.23 (d, J = 8.0 Hz, 3 H), 7.48−7.96 (m, 21 H); 1,2,4-isomer, δ 7.48−8.15 (m, 24 H). ^{13}C NMR: 1,3,5-isomer, δ 141.4 (3 C), 139.9 (3 C), 133.9 (3 C), 131.6 (3 C), 128.3 (3 CH), 128.0 (3 CH), 127.9 (3 CH), 127.1 (3 CH), 126.2 (3 CH), 125.9 (3 CH), 125.8 (3 CH), 125.4 (3 CH); 1,2,4-isomer:, δ 141.4 (C), 141.3 (C), 141.0 (C), 139.9 (C), 139.8 (C), 138.0 (C), 133.8 (C), 133.7 (C), 133.6 (C), 132.7 (C), 131.6 (C), 131.5 (C), 130.7 (CH), 128.5 (CH), 128.3 (2 CH), 128.2 (CH), 128.1 (CH), 128.0 (CH), 127.9 (2 CH), 127.8 (CH), 127.6 (CH), 127.2 (CH), 127.1 (CH), 126.4 (CH), 126.2 (CH), 126.1 (CH), 126.0 (2 CH), 125.8 (2 CH), 125.7 (CH), 125.5 (CH), 125.4 (2 CH). HRMS (EI, 70 eV): *m/z* $[M]^+$ calcd for $C_{36}H_{24}$ 456.1873, found 456.1881.

Tris(4-biphenyl)benzene (9).[38] 1-Ethynyl-4-biphenyl (178 mg) was used. White solid. Yield: 80%. ^{1}H NMR: 1,3,5-isomer, δ 7.91 (s, 3 H), 7.36−7.86 (m, 27 H); 1,2,4-isomer, δ 7.26−7.76 (m, 30 H). ^{13}C NMR: 1,3,5-isomer, δ 142.1 (3 C), 140.6 (3 C), 140.5 (3 C), 140.0 (3 CH), 128.8 (6 CH), 127.7 (6 CH), 127.6 (6 CH), 127.4 (6 CH), 127.1 (6 CH), 125.1 (3 CH); 1,2,4-isomer, δ 142.0 (C), 141.8 (C), 140.7 (C), 140.6 (C), 140.5 (C), 140.3 (C), 140.1 (C), 140.0 (C), 139.9 (C), 139.3 (C), 130.3 (3 C), 130.0 (3 CH), 128.7 (CH), (6 CH), 128.3 (3 CH), 127.7 (6 CH), 127.6 (6 CH), 127.5 (3 CH), 126.6, 125.7 (CH), 124.9 (CH). HRMS (EI, 70 eV): *m/z* $[M]^+$ calcd for $C_{42}H_{30}$ 534.2342, found 534.2363.

Tris(*n*-decyl)benzene (10).[39] Dodec-1-yne (2.14 mL) was used. Yellow liquid. Yield: 73%. ^{1}H NMR: 1,3,5-isomer, δ 6.82 (s, 3 H), 2.56 (m, 6 H), 1.52 (m, 6 H), 1.48−1.21 (m, 42 H), 0.88 (t, J = 6.6 Hz, 9 H); 1,2,4-isomer, δ 7.04 (d, J = 7.5 Hz, 1 H), 6.94 (s, 1 H), 6.92 (d, J = 7.5 Hz, 1 H), 2.48−2.61 (m, 6 H), 1.45−1.65 (m, 6 H), 1.20−1.43 (m, 42 H), 0.88 (m, 9 H). ^{13}C NMR: 1,3,5-isomer, δ 142.5 (3 C), 125.7 (3 CH), 31.6 (3 CH_2), 31.5 (3 CH_2), 31.3 (3 CH_2), 30.1 (3 CH_2), 29.1 (9 CH_2), 29.0 (3 CH_2), 22.5 (3 CH_2), 14.1 (3 CH_3); 1,2,4-isomer, δ 142.7 (C), 140.3 (C), 140.2 (C), 129.1 (CH), 128.8 (CH), 125.6 (CH), 36.0 (CH_2), 35.6 (CH_2), 32.8 (CH_2), 32.4 (CH_2), 31.9 (CH_2), 31.6 (CH_2), 31.62 (CH_2), 31.4 (CH_2), 29.9 (CH_2), 29.7 (CH_2), 29.6 (CH_2), 29.56 (3 CH_2), 29.5 (CH_2), 29.4 (3 CH_2), 29.1 (3 CH_2), 22.7 (3 CH_2), 22.6 (3 CH_2), 14.1 (3 CH_3). HRMS (EI, 70 eV): *m/z* $[M - CH_3]^+$ calcd for $C_{25}H_{63}$ 498.5159, found 498.5162.

Tris(1-cyclohexenyl)benzene (11).[36] 1-Ethynylcyclohex-1-ene (1.17 mL) was used. Yellow liquid. Yield: 67%. ^{1}H NMR: 1,3,5-isomer, δ 7.26 (s, 3 H), 6.06−6.14 (m, 3 H), 2.3−2.10 (m, 12 H), 1.64−1.59 (m, 12 H); 1,2,4-isomer, δ 7.19 (dd, J = 8.1, 2.1 Hz, 1 H), 7.13 (d, J = 2.1 Hz, 1 H), 7.04 (d, J = 8.1 Hz, 1 H), 6.06−6.14 (m, 1 H), 5.64−5.72 (m, 2 H), 2.04−2.48 (m, 12 H), 1.15−1.82 (m, 12 H). ^{13}C NMR: 1,3,5-isomer, δ 141.4 (6 C), 125.1 (3 CH), 120.9 (3 CH), 26.6 (3 CH_2), 23.5 (3 CH_2), 22.4 (3 CH_2), 22.1 (3 CH_2); 1,2,4-isomer, δ 143.1 (C), 140.2 (2 C), 139.6 (C), 137.7 (C), 136.9 (C), 129.0 (CH), 126.3 (CH), 125.8 (CH), 124.7 (CH), 123.4 (CH), 120.9 (CH), 30.1 (CH_2), 30.05 (CH_2), 29.5 (CH_2), 28.2 (CH_2), 26.4 (CH_2), 26.3 (CH_2), 26.1 (CH_2), 23.8 (CH_2), 23.6 (CH_2), 22.7 (CH_2), 22.6 (CH_2), 21.9 (CH_2). MS (EI 70 eV): *m/z* 318 (100, M), 237 (33), 179 (39), 165 (62), 141 (50), 81 (76), 79 (67).

Tris(4-(*N,N*-dimethylamino)phenyl)benzene (15).[40] 1-Ethynyl-4-dimethylaniline (1.45 g) was used. Pale yellow oil. Yield: 90%. ^{1}H NMR: 1,3,5-isomer, δ 3.07 (s, 18 H), 6.91 (d, J = 8.1 Hz, 6 H), 7.69 (d, J = 8.0 Hz, 6 H), 7.72 (s, 3 H); 1,2,4-isomer, δ 2.97 (s, 6 H), 2.98 (s, 6 H), 3.03 (s, 6 H), 6.69 (d, J = 7.8 Hz, 2 H), 6.71 (d, J = 7.7 Hz, 2 H), 6.87 (d, J = 9.1 Hz, 2 H), 7.17 (d, J = 7.8 Hz, 2 H), 7.20 (d, J = 7.8 Hz, 2 H), 7.48 (d, J = 7.9 Hz, 1 H), 7.59 (d, J = 8.0 Hz, 1 H), 7.63 (s, 1H), 7.66 (m, 2 H). ^{13}C NMR: 1,3,5-isomer, δ 41.6 (6 CH_3), 113.7 (3 CH), 123.5 (3 CH), 128.8 (3 CH), 130.7 (3 C), 142.9 (3 C), 150.9 (3 C); 1,2,4-isomer, δ 41.5 (2 CH_3), 41.6 (4 CH_3), 113.1 (6 CH), 125.4 (CH), 128.6 (2 CH), 129.4 (CH), 130.0 (C), 130.7 (C), 131.45 (2 CH), 131.50 (2 CH), 131.8 (C), 139.0 (C), 140.4 (C), 141.4 (C), 149.7 (C), 149.9 (C), 150.7 (C), 1 C is missing. HR-ESI-MS (positive ion mode): *m/z* $[M + H]^+$ calcd for $C_{30}H_{34}N_3$ 436.2753, found 436.2747.

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Supporting Information Available: Figures giving experimental and calculated HRMS spectra of the complex **B**. This material is available free of charge via the Internet at http://pubs.acs.org.

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