

Cyclotrimerization of Alkynes by Activated Metal Catalyst

Kyu Sang Choi, Moon Kyeu Park, and Byung Hee Han*

Department of Chemistry, College of Natural Sciences, Chungnam National University, Taejeon 305-764, Korea

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Activated metal powders, prepared by the reduction of the corresponding metal halide with alkali metals in an ethereal solvent, have been employed in a wide variety of synthetic applications.¹ However, no example has been reported for the cyclotrimerization of alkynes using activated metal powders prepared by this method. Literature deals mainly with metal carbonyls,² late transition metal complexes,³ early transition metal complexes,⁴ Ziegler catalyst,⁵ trialkylphosphine,⁶ organolanthanide⁷ and organoactinide complexes⁸ for the cyclotrimerization of alkynes. It was also shown that some of the metal (Nb, Ta, Mo, Ni, W) halides,⁹ Pd with CH₃SiCl₃,¹⁰ the combination of Zn-TaCl₅¹¹ and the atomized metals (Fe, Cu, Cr, Co)¹² can act as catalysts. The production of benzene from ethyne was also observed over other metals as well, for example, over Pd on alumina,¹³ crystal Pd(111)¹⁴ and Sn/Pt.¹⁵ The reactivity of ethyne with late transition metals has been extensively established¹⁶ and cyclotrimerization is a common reaction pathway. Despite of the reactivity of early transition metals¹⁷ for the formation of benzene from ethyne has been explored, cyclic trimerization of internal alkynes to substituted benzenes is rarely observed. Many of these methods produce complex reaction mixtures, which afford low yields of the desired trimers while all require very stringent reaction conditions. The development of a more convenient method for the trimerization of alkynes is therefore still desirable.

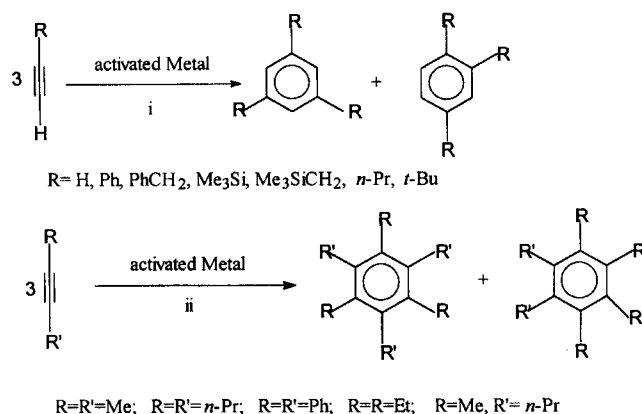
We recently reported that activated metals catalyze the hydrosilylation of carbonyls,¹⁸ and olefins,^{18,19} the reduction of nitroarenes²⁰ and the coupling of carbonyls.²¹ During the attempted addition of an alkylsilane to alkynes, we observed that an activated zirconium-titanium, prepared by the reduction of zirconium tetrachloride and titanium trichloride with lithium powder showed the exceptional catalytic activity for the formation of 1,2,4 and 1,3,5-triphenylbenzenes from phenylacetylene in high yields.²² In continuation of our work, we decided to study the reactivity of various activated metal catalysts as well as activated zirconium-titanium catalyst for cyclotrimerization of terminal alkynes, internal alkynes and asymmetric alkynes. The results of the cyclotrimerization of the alkynes with these catalysts are summarized in Table 1.

We found that using activated metals, such as Ni, Ti, Cr, Fe, Mn, Mo, MoO, and W, triphenylbenzenes (1,2,4- and 1,3,5-isomers) were formed in 80-88% isolated yields (using Ni, MoO and Mo) (runs 1-3), 5-20% by GLC (using Fe, Cr, Mn) (runs 4-6), 10-55% yield together with the hydrogenated dimer, 1,4-diphenylbutane in 44-56% (using W, Ti and Nb) (runs 7-9) and unreacted phenylacetylene as well (by GLC). However, these activated metal catalysts were inactive for internal alkynes, such as 3-hexyne. Activated titanium catalyst can be prepared by the reaction of titanium trichloride with zinc or magnesium instead of lithium in THF (runs 10-11). Cyclotrimerization of phenylacetylene did

not occur using a commercially purchased zirconium (or titanium) in DME/THF and refluxed under nitrogen for 6 h (run 13c). Cyclotrimerization was not also detected at all and most of the phenylacetylene was recovered when zirconium tetrachloride, titanium trichloride and phenylacetylene was refluxed in DME/THF for 8 h.

Meanwhile, activated zirconium catalyzed the cyclotrimerization of 3-phenyl-1-propyne and phenylacetylene to afford the corresponding trisubstituted benzene derivatives in 85% and 95% isolated yields (combined yields of 1,3,5 and 1,2,4 isomers) respectively (runs 12-13). However, using activated Zr or Ti, the cyclotrimerization of 3,3-dimethyl-1-butyne, (trimethylsilyl)acetylene and 1-pentyne as well as internal alkynes were not successful. For the 1,3,5 versus 1,2,4 isomer ratio using activated metals, such as Zr, MoO and Zr-Ti, the 1,3,5-trisubstituted benzenes were the major products as expected in the case of phenylacetylene (runs 2, 13), trimethylsilylacetylene (run 19), 1-pentyne (run 20) and 3,3-dimethyl-1-butyne (run 21). Interestingly, the more hindered 1,2,4-isomers were the major products using activated Ni, Mo, W, Nb, Ti and Zr-Ti in the case of phenylacetylene (runs 1, 3, 7-11), 3-phenyl-1-propyne (runs 12, 18), 3-(trimethylsilyl)-1-propyne (run 22) and 2-hexyne (run 24) under the same reaction conditions.

Using activated Zr-Ti catalysts, the terminal alkynes as well as internal alkynes (such as R-C≡C-R', R=R'=Me; R=R'=Et; R=R'=n-Pr; R=R'=Ph; R=Me, R'=Et) were mainly cyclotrimerized to the 1,2,4 and 1,3,5-benzene derivatives in fair yield without the formation of a dimer or polymer (run 24-27). However, the cyclotrimerization of internal alkynes,



Scheme 1. Reagents and conditions: Activated metal was prepared by the reduction of metal halide with Li powder in DME/THF (stirred 1 h for metal activation); for more details, see Experimental section. i, After metal activation, alkyne (10 mmol) was added and stirred at 25 °C or refluxed again for 3 h; ii, After metal activation, alkyne (10 mmol) was added and stirred again at 25 °C or refluxed for 3 h.

Table 1. Activated metal catalyzed cyclotrimerization of alkynes^a

Run	Activated metal	Metal halide activation condition	Solvent	R \equiv R'	Reaction condition	Yield ^b (% isolated)	1,3,5 : 1,2,4 isomers ratio
1	Ni	NiI ₂ , Li, Stir, 1h	THF	R=Ph, R'=H	Reflux, 3 h	83	0.2 : 1
2	MoO	MoOCl ₄ , Zn, Reflux, 1h	DME	R=Ph, R'=H	Reflux, 3 h	88	2.1 : 1
3	Mo	MoCl ₅ , Zn, Reflux, 1h	THF	R=Ph, R'=H	Stir, 6 h	80	0.6 : 1
4	Fe	FeCl ₃ , Li, Reflux, 3 h	DME/THF	R=Ph, R'=H	Reflux, 3 h	13 ^d	
5	Cr	CrCl ₃ , Li, Reflux, 3 h	DME/THF	R=Ph, R'=H	Reflux, 3 h	20 ^d	
6	Mn	MnCl ₂ , Li, Reflux, 3 h	DME/THF	R=Ph, R'=H	Reflux, 3 h	5 ^d	
7	W	WCl ₆ , Li, Stir, 1 h	THF	R=Ph, R'=H	Reflux, 6 h	55 ^d , 45 ^e	0.83 : 1
8	Nb	NbCl ₅ , Li, Stir, 1 h	THF	R=Ph, R'=H	Reflux, 3 h	44 ^d , 56 ^e	0.85
9	Ti	Ti Cl ₃ , Li, Stir, 1 h	DME	R=Ph, R'=H	Stir, 3 h	56 ^d , 44 ^e	0.81 : 1
10	Ti ^f	Ti Cl ₃ , Zn, Stir, 1 h	THF	R=Ph, R'=H	Reflux, 4 h	85	0.4 : 1
11	Ti ^f	Ti Cl ₃ , Mg, Stir, 1 h	THF	R=Ph, R'=H	Reflux, 3 h	90	0.15 : 1
12	Zr	ZrCl ₄ , Li, Stir, 1h	THF	R=PhCH ₂ , R'=H	Stir, 3 h	85	0.3 : 1
13	Zr	ZrCl ₄ , Li, Stir, 1 h	THF	R=Ph, R'=H	Stir, 3 r	95, 0 ^g	1.38 : 1
14	Zr	ZrCl ₄ , Li, Stir, 1 h	DME/THF	R=tert-Bu, R'=H	Stir, 3 h	35 ^d , 20 ^g	
15	Zr	ZrCl ₄ , Li, S tir, 1 h	DME/THF	R=H, R'=H	Stir, 6 h	No reaction	
16	Ti	Ti Cl ₃ , Mg, S tir, 1 h	THF	R=H, R'=H	Stir, 6 h	No reaction	
17	Ti	Ti Cl ₃ , Zn, Stir, 1 h	THF	R=Et ₃ Si R'=H	Reflux, 6 h	No reaction	
18	Zr-Ti	ZrCl ₄ , TiCl ₃ , Li, Stir, 1h	THF	R=PhCH ₂ , R'=H	Stir, 3 h	93	0.39 : 1
19	Zr-Ti	ZrCl ₄ , TiCl ₃ , Li, Stir, 1 h	DME/THF	R=Me ₃ Si, R'=H	Stir, 3 h	82	15.7 : 1
20	Zr-Ti	ZrCl ₄ , TiCl ₃ , Li, Stir, 1 h	DME/THF	R=n-Pr, R'=H	Stir, 3 h	83	1.7 : 1
21	Zr-Ti	ZrCl ₄ , TiCl ₃ , Li, Stir, 1 h	DME/THF	R=tert-Bu, R'=H	Stir, 3 h	79	7.33 : 1
22	Zr-Ti	ZrCl ₄ , TiCl ₃ , Li, Stir, 1 h	DME/THF	R=Me ₃ SiCH ₂ , R'=H	Stir, 3 h	71	0.52 : 1
23	Zr-Ti	ZrCl ₄ , TiCl ₃ , Li, Stir, 1 h	DME/THF	R=R'=H	Stir, 3 h	Detected h	
24	Zr-Ti	ZrCl ₄ , TiCl ₃ , Li, Stir, 1 h	DME/THF	R=n-Pr, R'=Me	Stir, 2 h	73	0.43 : 1
25	Zr-Ti	ZrCl ₄ , TiCl ₃ , Li, Stir, 1 h	DME/THF	R=R'=Me	Stir, 2 h	82	
26	Zr-Ti	ZrCl ₄ , TiCl ₃ , Li, Stir, 1 h	DME/THF	R=R'=n-Pr	Stir, 3 h	81	
27	Zr-Ti	ZrCl ₄ , TiCl ₃ , Li, Stir, 1 h	DME/THF	R=R'=Ph	Neat, ⁱ 150 °C, 12 h	60	
28	Zr-Ti	ZrCl ₄ , TiCl ₃ , Li, Stir, 1 h	DME/THF	R=Ph, R'=Me	Reflux, 2 h	No reaction	
29	Zr-Ti	ZrCl ₄ , TiCl ₃ , Li, Stir, 1 h	DME/THF	R=Ph, R'=SiMe ₃	Reflux, 2 h	No reaction	
30	Zr-Ti	ZrCl ₄ , TiCl ₃ , Li, Stir, 1 h	DME/THF	R=Me, R'=SiMe ₃	Reflux, 2 h	No reaction	
31	Zr-Ti	ZrCl ₄ , TiCl ₃ , Li, Stir, 1 h	DME/THF	R=R'=COOMe	Reflux, 6 h	No reaction	
32	Zr-Ti	ZrCl ₄ , TiCl ₃ , Li, Stir, 1 h	DME/THF	R= Me ₃ Si, R'=SiMe ₃	Reflux, 6 h	No reaction	
33	Zr-Ti	ZrCl ₄ , TiCl ₃ , Li, Stir, 1 h	DME/THF	R=Me ₂ NCH ₂ , R'=H	Reflux, 3 h	No reaction	
34	Zr-Ti	ZrCl ₄ , TiCl ₃ , Li, Stir, 1 h	DME/THF	R=HOCH ₂ , R'=H	Reflux, 6 h	No reaction	
35	Zr-Ti	ZrCl ₄ , TiCl ₃ , Li, Stir, 1 h	DME/THF	R=N≡C (CH ₂) ₃ , R'=H	Reflux, 6 h	No reaction	

^a Activated metals were prepared by the reaction of the corresponding metal halides with alkali metals in THF or dimethoxyethane (4 mL)/tetrahydrofuran (1 mL). ^b In the case of a mixture of isomers; isomers ratio are cited. ^c Using commercially available Zr, Ti and Zr-Ti (refluxed, 6 h). ^d GC yield. ^e Hydrogenated dimer, 1,4-diphenylbutane was formed by GC-Mass. ^f TiCl₃ (2 mmol) and metal (3 mmol) in THF (5 mL) were employed for metal activation. ^g 1,4-Di-*tert*-butyl-1,3-butadiene was formed by GC-Mass. ^h Identified by NMR and GLC-Mass. ⁱ After activation, solvent was evaporated and 1,2-diphenylacetylene was added.

(such as R-C≡C-R', R=Ph, R'=Me; R=Ph, R'=SiMe₃; R=Me, R'=SiMe₃; R=SiMe₃, R'=SiMe₃; R=R'=COOMe), did not occur using an activated Zr-Ti catalysts (runs 28-32).

We have studied the reactivity of activated metal co-catalysts system. Surprisingly, it appears that titanium is the best choice of a metal for the preparation of catalysts with zirconium. For example, the cyclotrimerization of 3,3-dimethyl-1-butyne using activated Zr-Ti gave 1,3,5 and 1,2,4-tri-*tert*-butylbenzenes in 79% isolated yield (1,3,5/1,2,4=7.33/1; isomer ratio) (run 21). However, when the same reaction was carried out using activated zirconium alone, tri-*tert*-butylbenzene was formed in 35% yields (1,3,5/1,2,4=4/1; isomer ratio) along with a dimer, 1,4-di-*tert*-butyl-1,3-butadiene in 20% yield and unidentified compounds (by GLC) (run 14). The cyclotrimerization of 3,3-dimethyl-1-butyne using activated titanium under the same reaction

conditions gave much poor yields along with unidentified products. Also, the yields for the cyclotrimerization of 3,3-dimethyl-1-butyne were not improved when the other activated catalysts prepared from a mixture of ZrCl₄ and metal halides (such as NiI₂, WCl₆, CrCl₃, FeCl₃, MnCl₂, MoCl₅) with Li powder (stirred 1 h for metal activation, stirred or refluxed 2-6 h for cyclotrimerization) were employed. Meanwhile, the cyclotrimerization of ethyne to benzene using activated Zr-Ti was very successful (more in details, see experimental). However, the attempted cyclotrimerization of ethyne to benzene using activated Fe, Cr, Mo, Mn, Zr, Ni, W or Ti under the same reaction conditions were unsuccessful (such as runs 15-16). The attempted cyclotrimerization of amine and alcohol substituted alkynes using activated metals did not occur (runs 33-36). The source of this reactivity of the highly activated metal species in the cyclotrimerization

of alkynes may be the high surface area, some unique metal species.

In conclusion, we have demonstrated that activated metal powder provides the cyclotrimerization of alkynes. Efforts are being made to apply these highly reactive metal powders to the cyclotrimerization of diynes as well as to the transformation of the organic functional groups.

Experimental

Anhydrous metal halides and alkynes were purchased from Aldrich, Junsei and Yakuri and used without further purification. Tetrahydrofuran (THF) and dimethoxyethane (DME) were distilled under nitrogen from sodium/benzophenone ketyl before use. High quality hydrocarbon solvents such as hexane or pentane were obtained by stirring the sulfuric acid for 3 days followed by distillation. Lithium powder (99%) was purchased from Aldrich Chemicals. ^1H NMR spectra were obtained on a Varian Inova 400 spectrometer. Chemical shifts were reported in ppm downfield from TMS and coupling constants were obtained from first order analysis of the spectra. Mass spectra (70 eV electron impact) were taken on a Finnigan 4510 instrument equipped with a Finnigan-incos data system and Jeol MS-SX102A system. Melting points were determined with an Electrothermal apparatus and were uncorrected. GLC analyses were carried out on a Varian 3300 Model equipped with a FID detector and stainless steel column packed with 10% OV-101, Chromosob W HP 80/100 (2 m \times 1/8 in). Flash column chromatography was carried out on Merck silica gel 60 (70-230 mesh). Thin layer chromatography was performed on silica gel plate (E. Merck, 60, No. 5539).

General Procedure for the Preparation of Activated Zirconium Metal Powders. In a glove box, a 100 mL two-neck round bottom flask, equipped with a magnetic stirrer and a condenser topped with a nitrogen inlet, was charged with ZrCl_4 (0.23 g, 1 mmol), Li powder (0.029 g, 4.2 mmol) and freshly distilled THF (5 mL) was syringed into the flask. After stirring these reagents under an atmosphere of nitrogen at room temperature for 1 h, the finely divided metal appeared as black powders, which settled, in a dark solution. The activated zirconium in a dark solution was used in this investigation without any further treatment.

General Procedure for the Preparation of Activated Zirconium-titanium Metal Powders. In a nitrogen atmospheric glove box, a 100 mL two-neck round bottom flask, equipped with a magnetic stirrer and a condenser topped with a nitrogen inlet, was charged with ZrCl_4 (0.23 g, 1 mmol), TiCl_3 (0.15 g, 1 mmol), Li powder (0.053 g, 7.5 mmol) and freshly distilled DME (4 mL) and THF (1 mL) were syringed into the flask. After stirring these reagents under an atmosphere of nitrogen at room temperature for 1 h, the finely divided metal appeared as black powders that settled in a dark solution. The activated zirconium-titanium in a dark solution was used in this investigation without any further treatment.

Typical Procedure: Cyclotrimerization of Phenylacetylene Activated zirconium-titanium was Illustrated. Activated zirconium-titanium in a dark solution (mentioned above) was charged with phenylacetylene (1.1

mL, 10 mmol). The mixture was stirred under nitrogen for 3 h. Product isolation was straightforward. After 3 h, the solvent was evaporated and dichloromethane was added. The solution was filtered to remove the catalyst through a pad of silica gel column (1 cm diameter \times 5 cm packed) using hexane-dichloromethane (1:1, v/v) as an eluent. Solvent evaporation yields a mixture (0.97 g, 95%) of 1,3,5-triphenylbenzene (58%) and 1,2,4-triphenylbenzene (42%). The isolated yields are based on quantities obtained after this step. Isomers yielded (also given by isomers ratio; see Table 1) are based on GLC analysis and authentic samples. 1,2,4-Trisubstituted benzene has lower retention time than 1,3,5-trisubstituted benzene on GLC in all cases.

Selected ^1H NMR (CDCl_3), δ 7.10-7.30 (m, aromatic-H, 1, 3,5- and 1,2,4- $\text{Ph}_3\text{C}_6\text{H}_3$), 7.40 (d, $J=4.4$ Hz, 1H, 1,2,4-CPh-CPhCHCPhCHCH), 7.52 (d, $J=4.4$ Hz, 1H, 1,2,4-CPh-CPhCHCPhCHCH), 7.70 (s, 1H, 1,2,4-CPhCPhCHCPhCHCH), 7.78 (s, 3H, 1,3,5- $\text{Ph}_3\text{C}_6\text{H}_3$); $1,3,5\text{-Ph}_3\text{C}_6\text{H}_3$, m/z (EI) 306 (M^+ , 100), 229 (2), 151 (2); $1,2,4\text{-Ph}_3\text{C}_6\text{H}_3$, m/z (EI), 306 (M^+ , 100), 229 (7), 151 (4), 77 (2).

Cyclotrimerization of Phenylacetylene using Activated W, Ti and Nb. Cyclotrimerization of phenylacetylene with activated metals, such as W, Ti and Nb gave the hydrogenated 1,4-diphenylbutane (44-56%) along with 1,3,5 and 1,2,4-triphenylbenzene (44-56%) (by GLC).

$1,4\text{-Ph}_2\text{C}_4\text{H}_8$, m/z (EI), 210 (M^+ , 49), 117 (13), 91 (100), 65 (19).

Some spectral properties of the cyclotrimerized products of alkynes are as follows.

1,3,5-Tribenzylbenzene and 1,2,4-tribenzylbenzene from 3-phenyl-1-propyne. Selected ^1H NMR (CDCl_3), δ 3.88 (s, 6H, 1,3,5-(PhCH_2) $_3\text{C}_6\text{H}_3$), 3.89 (s), 3.90 (s), 3.93 (s, 6H, three CH_2 , 1,2,4-(PhCH_2) $_3\text{C}_6\text{H}_3$), 6.80-7.06 (m, 6H, aromatic-H, 1,3,5- and 1,2,4-(PhCH_2) $_3\text{C}_6\text{H}_3$), 7.16 (d, $J=2.01$ Hz, 1H, 1,2,4- $\text{PhCH}_2\text{CPhCH}_2\text{CCHPhCH}_2\text{CCHCH}$), 7.22 (d, $J=2.01$ Hz, 1H, 1,2,4- $\text{PhCH}_2\text{CPhCH}_2\text{CCHPhCH}_2\text{CCHCH}$), 7.25 (s, 1H, 1,2,4- $\text{PhCH}_2\text{CPhCH}_2\text{CHCPhCH}_2\text{CCHCH}$), 7.26 (s, 3H, 1,3,5-(PhCH_2) $_3\text{C}_6\text{H}_3$); $1,3,5\text{-(PhCH}_2)_3\text{C}_6\text{H}_3$, m/z (EI), 348 (M^+ , 77), 257 (40), 179 (100), 91 (45); $1,2,4\text{-(PhCH}_2)_3\text{C}_6\text{H}_3$, m/z (EI), 348 (M^+ , 89), 257 (100), 179 (31), 91 (51).

1,3,5-Tris(trimethylsilyl)benzene and 1,2,4-tris(trimethylsilyl)benzene from (trimethylsilyl)acetylene. Selected ^1H NMR (CDCl_3), δ 0.20 (s, 27H, 1,3,5-(Me_3Si) $_3\text{C}_6\text{H}_3$), 0.28 (s), 0.29 (s), 0.30 (s), (s, 27H, three Me_3Si , 1,2,4-(Me_3Si) $_3\text{C}_6\text{H}_3$), 7.60-7.41 (m, 3H, 1,2,4-(Me_3Si) $_3\text{C}_6\text{H}_3$, *ortho* $^3J=7.5$ Hz), 7.77 (s, 1,3,5-(Me_3Si) $_3\text{C}_6\text{H}_3$); $1,3,5\text{-(Me}_3\text{Si})_3\text{C}_6\text{H}_3$, m/z (EI), 294 (M^+ , 13), 279 (60), 263 (55), 191 (38), 73 (100), 45 (32); $1,2,4\text{-(Me}_3\text{Si})_3\text{C}_6\text{H}_3$, m/z (EI), 294 (M^+ , 11), 279 (100), 132 (13), 73 (34).

1,3,5-Tris(trimethylsilylmethyl)benzene and 1,2,4-tris(trimethylsilylmethyl)benzene from 3-(trimethylsilyl)-1-propyne. Selected ^1H NMR (CDCl_3), δ 0.01 (s, 27H, 1,3,5-(Me_3SiCH_2) $_3\text{C}_6\text{H}_3$), 0.02 (s), 0.04 (s), 0.06 (s, 27H, three Me_3Si , 1,2,4-(Me_3SiCH_2) $_3\text{C}_6\text{H}_3$), 1.92 (s, 6H, 1,3,5-(Me_3SiCH_2) $_3\text{C}_6\text{H}_3$), 1.966 (s), 1.97 (s), 1.98 (s, 6H, three CH_2 , 1,2,4-(Me_3SiCH_2) $_3\text{C}_6\text{H}_3$), 6.34 (s, 3H, 1,3,5-(Me_3SiCH_2) $_3\text{C}_6\text{H}_3$), 6.60 (s, 1H, 1,2,4- $\text{Me}_3\text{SiCH}_2\text{CMe}_3\text{SiCH}_2\text{CHCMe}_3\text{SiCH}_2\text{CCHCH}$), 6.62 (d, $^3J=7.54$ Hz, 1,2,4- $\text{Me}_3\text{SiCH}_2\text{CMe}_3\text{SiCH}_2\text{CCHCH}$), 6.78 (d, *ortho*, $^3J=7.54$ Hz, 1,2,4- $\text{Me}_3\text{SiCH}_2\text{CMe}_3\text{SiCH}_2\text{CCHCH}$); $1,3,5\text{-(Me}_3\text{SiCH}_2)_3\text{C}_6\text{H}_3$, m/z (EI), 348 (M^+ , 77), 257 (40), 179 (100), 91 (45); $1,2,4\text{-(Me}_3\text{SiCH}_2)_3\text{C}_6\text{H}_3$, m/z (EI), 348 (M^+ , 89), 257 (100), 179 (31), 91 (51).

(Me_3SiCH_2), C_6H_5 , m/z (EI), 336 (M^+ , 15), 73 (100), 45 (15); $1,2,4$ -(Me_3SiCH_2) $_3\text{C}_6\text{H}_5$, m/z (EI), 336 (M^+ , 21), 263 (2), 73 (100), 45 (15).

1,3,5-Tri-*n*-propylbenzene and 1,2,4-tri-*n*-propylbenzene from 1-pentyne. Selected ^1H NMR (CDCl_3), δ 6.81 (s, 3H, 1,3,5-($n\text{-C}_3\text{H}_7$) $_3\text{C}_6\text{H}_3$), 6.90-7.08 (m, 3H, 1,2,4-($n\text{-C}_3\text{H}_7$) $_3\text{C}_6\text{H}_3$); $1,3,5$ -($n\text{-C}_3\text{H}_7$) $_3\text{C}_6\text{H}_3$, m/z (EI), 204 (M^+ , 35), 175 (100), 147 (32), 105 (38), 91 (19); $1,2,4$ -($n\text{-C}_3\text{H}_7$) $_3\text{C}_6\text{H}_3$, m/z (EI), 204 (M^+ , 30), 175 (100), 147 (7), 105 (13), 91 (2).

1,3,5-Tri-*tert*-butylbenzene and 1,2,4-tri-*tert*-butylbenzene from 3,3-dimethyl-1-butyne. Selected ^1H NMR (CDCl_3), δ 1.31 (s, 27H, three *t*-Bu, 1,3,5-(Me_3C) $_3\text{C}_6\text{H}_3$), 1.53 (s), 1.54 (s), 1.56 (s, 27H, three *t*-Bu, 1,2,4-(Me_3C) $_3\text{C}_6\text{H}_3$), 7.12 (dd, $J=2.3$ Hz, 8.49 Hz, 2H, 1,2,4-(Me_3C) $_3\text{C}(\text{Me}_3\text{C})_3\text{CCH}(\text{Me}_3\text{C})_3\text{CCHCH}$), 7.45 (s, 3H, 1,3,5-(Me_3C) $_3\text{C}_6\text{H}_3$), 7.56 (s, 1H, 1,2,4-(Me_3C) $_3\text{C}(\text{Me}_3\text{C})_3\text{CCH}(\text{Me}_3\text{C})_3\text{CCHCH}$); $1,3,5$ -(Me_3C) $_3\text{C}_6\text{H}_3$, m/z (EI), 246 (M^+ , 43), 231 (43), 175 (13), 105 (5), 57 (100); $1,2,4$ -(Me_3C) $_3\text{C}_6\text{H}_3$, m/z (EI), 246 (M^+ , 11), 231 (100), 57 (45).

Cyclotrimerization of 3,3-dimethyl-1-butyne using activated Ti or Zr alone gave 1,4-di-*tert*-butyl-1,3-butadiene (44-56%) along with 1,3,5-tri-*tert*-butylbenzene and 1,2,4-tri-*tert*-butylbenzene by GC-MS.

$1,4$ -Di-(*tert*- C_4H_9) $_2\text{-C}_4\text{H}_6$, m/z (EI), 166 (M^+ , 38), 151 (32), 123 (72), 109 (100), 95 (58), 81 (32), 67 (43), 41 (55).

1,3,5-Trimethyl-2,4,6-tri-*n*-propylbenzene and 1,2,4-trimethyl-3,5,6-tri-*n*-propylbenzene from 2-hexyne. Selected ^1H NMR (CDCl_3), δ 0.93-1.10 (t, $J=6.97$, 9H, 1,3,5- CH_3 , and t, $J=6.97$, 9H, 1,2,4- CH_3), 1.27-1.63 (m, 12H, 1,3,5- CH_2 and 1,2,4- CH_2), 2.20 (s, 9H, 1,2,4-aromatic- CH_3), 2.24 (s, 3H, 1,3,5-aromatic- CH_3), 2.48-2.71 (t, $J=6.97$, 6H, 1,3,5-aromatic- CH_2 and t, $J=6.97$, 6H, 1,2,4-aromatic- CH_2); $1,3,5$ -(CH_3) $_3\text{-2,4,6}$ -($n\text{-C}_3\text{H}_7$) $_3\text{C}_6$, m/z (EI), 246 (M^+ , 32), 217 (100), 175 (8), 147 (13), 133 (11), 41 (6); $1,2,4$ -(CH_3) $_3\text{-3,5,6}$ -($n\text{-C}_3\text{H}_7$) $_3\text{C}_6$, m/z (EI), 246 (M^+ , 32), 217 (100), 175 (34), 147 (19), 133 (17), 41 (9).

Hexaethylbenzene from 3-hexyne. ^1H NMR (CDCl_3), δ 1.2 (t, $J=7.6$ Hz, 3H, CH_3), 2.63 (q, $J=7.6$ Hz, CH_2); m/z (EI), 246 (M^+ , 53), 231 (100); mp 129 °C (lit.²³, 130 °C).

Hexamethylbenzene from 2-butyne. ^1H NMR (CDCl_3), δ 2.23 (s, CH_3); m/z (EI), 162 (M^+ , 45), 147 (100), 91 (10); mp 168 °C (lit.²⁴, 165-166 °C).

Hexa-*n*-propylbenzene from 4-octyne. ^1H NMR (CDCl_3), δ 1.04 (t, $J=3.58$ Hz, 3H, $-\text{CH}_3$), 1.52 (m, 2H, $-\text{CH}_2-$), 2.47 (t, $J=3.58$ Hz, 2H, aromatic- CH_2-); m/z (EI), 330 (M^+ , 45), 301 (100), 259 (6), 217 (13), 175 (21), 145 (13), 105 (13), 43 (57); mp 101-102 °C (lit.²⁴ mp 101.5-102 °C).

Hexaphenylbenzene from Diphenylacetylene. In a glove box, a 100 mL two-neck round bottom flask, equipped with a magnetic stirrer and a condenser topped with a nitrogen inlet, was charged with ZrCl_4 (0.23 g, 1 mmol), TiCl_3 (0.15 g, 1 mmol), Li powder (0.053 g, 7.5 mmol) and freshly distilled DME (4 mL) and THF (1 mL) were syringed into the flask. After stirring these reagents under a atmosphere nitrogen at room temperature for 1 h, the finely divided metal appeared as black powders which settled in a dark solution. Solvent was removed under reduced pressure and diphenylacetylene (0.89 g, 5 mmol) was added. Reaction mixture was heated at 150 °C using mantle with sand for 12 h. After cooling to room

temperature, dichloromethane was added. The solution was filtered to remove the catalyst through a pad of silica gel column (1 cm dia. \times 25 cm packed) using dichloromethane as an eluent. Solvent evaporation yields white solid of hexaphenylbenzene (0.53 g, 60%). ^1H NMR (CDCl_3), δ 6.83 (s, 5H, aromatic-H); m/z (EI), 534 (M^+ , 100); mp 438 °C (lit.²⁴, 454 °C).

Benzene from Ethyne. In a glove box, a 100 mL two-neck round bottom flask, equipped with a magnetic stirrer and a condenser topped with a nitrogen inlet, was charged with ZrCl_4 (0.23 g, 1 mmol), TiCl_3 (0.15 g, 1 mmol), Li powder (0.053 g, 7.5 mmol) and freshly distilled DME (4 mL) and THF (1 mL) were syringed into the flask. After stirring these reagents under an atmosphere of nitrogen at room temperature for 1 h, the finely divided metal appeared as black powders which settled in a dark solution. These reagents were stirred again under an atmosphere of ethyne using balloon at room temperature for 3 h. The mixture was filtered and the remaining liquid on fractionation yielded benzene (0.1 mL). ^1H NMR (CDCl_3), δ 7.4 (s); m/z (EI), 78 (M^+ , 100).

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