# **ORGANOMETALLICS**

# Silica-Supported Tungsten Carbynes ( $\equiv$ SiO)<sub>x</sub>W( $\equiv$ CH)(Me)<sub>y</sub> (x = 1, y = 2; x = 2, y = 1): New Efficient Catalysts for Alkyne Cyclotrimerization

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**S** Supporting Information

**ABSTRACT:** The activity of silica-supported tungsten carbyne complexes  $(\equiv SiO)_x W(\equiv CH)(Me)_y$  (x = 1, y = 2; x = 2, y = 1) toward alkynes is reported. We found that they are efficient precatalysts for terminal alkyne cyclotrimerization with high TONs. We also demonstrate that this catalyst species is active for alkyne cyclotrimerization without the formation of significant alkyne metathesis products. Additional DFT calculations highlight the importance of the W coordination sphere in supporting this experimental behavior.



# INTRODUCTION

Cyclotrimerization  $\begin{bmatrix} 2 + 2 + 2 \end{bmatrix}$  of alkynes catalyzed by transition metals is an elegant chemical transformation for the single-step construction of multiply substituted aromatic compounds. This reaction, discovered by Berthelot in 1866, refers to the addition of three acetylene molecules to form benzene derivatives at very high temperatures.<sup>1</sup> Later on, Reppe found that the transition-metal complex Ni(CO)<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> could efficiently catalyze this reaction.<sup>2</sup> Since then, numerous procedures employing late transition metals rather than earlier transition metals have been reported for this alkyne cyclotrimerization.<sup>3-5</sup> In particular, the use of group VI precursors in their high oxidation state is scarce. In the late 1960s, Boelhouwer and co-workers<sup>6</sup> reported the cyclotrimerization of alkyne catalyzed by silica-supported tungsten trioxide, which was originally the catalyst used by Bailey and Banks for the first report on alkyne metathesis.<sup>6,7</sup> In a fixed bed reactor, 1-pentyne (WHSV, 1-4 h<sup>-1</sup>) is transformed into tripropylbenzene derivatives at high temperatures (>250 °C). However, no mechanism was proposed to elucidate how the d<sup>0</sup> W<sup>VI</sup> species in its high oxidation state could be active for alkyne cyclotrimerization. Thus, the late development of surface organometallic chemistry, in which an organometallic precursor is grafted in a controlled manner at the surface of an oxide, proved to be an ideal tool to reach a better fundamental understanding of heterogeneous catalysis.8 For instance, the design and synthesis of numerous well-defined silica-supported

tungsten oxo alkyl precursor complexes gave more insights to improve the catalyst performance for olefin metathesis.<sup>9</sup> Ensuing this strategy, we reported recently the characterization of supported  $\equiv$ Si-O-WMe<sub>5</sub> (1), which upon thermal treatment at ca. 150 °C evolves to the unprecedented W methylidyne/methyl species 2 (Scheme 1).<sup>10</sup>

Scheme 1. Transformation of  $\equiv$ Si-O-WMe<sub>5</sub> (1) into ( $\equiv$ SiO)<sub>x</sub>W( $\equiv$ CH)(Me)<sub>y</sub> (2: x = 1, y = 2; x = 2, y = 1)



Following the isolation of this thermally stable W species 2, we decided to examine its activity toward alkynes. In our recent work, we observed an equilibrium between 2 and W bismethylidene promoted by coordination of either  $PMe_3$  or an olefin to 2.<sup>11</sup> Moreover, it was demonstrated earlier that the use of bis-alkoxide alkylidyne species instead of a bis-alkyl alkylidyne is required to achieve alkyne metathesis, highlighting the importance of the W coordination sphere.<sup>12</sup> Herein we

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report the remarkable activity of supported complexes 1 and 2 for the alkyne cyclotrimerization and provide the origin of such reactivity toward alkyne metathesis by DFT calculations.

# RESULTS AND DISCUSSION

In a sealed tube, a catalytic amount of 1 or 2 was allowed to react with 1-hexyne at 150 °C. Cyclotrimerization of 1-hexyne catalyzed by either 1 or 2 gave a mixture of the two aromatic regioisomers 1,3,5-tri-*n*-butylbenzene (3a) and 1,2,4-tri-*n*-butylbenzene (3b) in quantitative yield with a molar ratio of 29:71, respectively (Scheme 2).





The structure of these regioisomers was further confirmed by NMR spectroscopy. In <sup>1</sup>H NMR spectroscopy, the signal at 6.82 ppm corresponds to the three equivalent protons bonded to  $sp^2$  carbons of the aromatic rings of 3a, while the set of signals at 6.93-6.95 and 7.05 ppm accounts for the CH aromatic resonances of 3b. GC-MS and high-resolution mass spectroscopy further confirmed the molecular weight of these aromatic compounds. No polymeric products were observed at the end of the catalytic run, as determined by the absence of proton resonances between 5 and 6 ppm. Furthermore, aromatic products 4 with an electron ionization fragment of m/z 302 were also observed (molar fraction <2%). We suggest that these products 4 are obtained from the cross-cyclotrimerization of two molecules of 1-hexyne and one molecule of 5-decyne, in comparison to 1-hexyne cyclotrimerization producing 3. The formation of 5-decyne would imply that an initial 1-hexyne homometathesis reaction occurs as a competitive pathway of alkyne cyclotrimerization. The general mechanism for alkyne metathesis proposed by Katz involves the [2 + 2] cycloaddition of an alkyne and a metal carbyne via a metallacyclobutadiene intermediate.<sup>13</sup> In the presence of terminal alkyne, the latter then undergoes cycloreversion to produce either ethyne and W alkylidyne or the starting alkyne as a degenerative step. Thus, 1-hexyne metathesis catalyzed by 2 would give 5-decyne, as shown in Scheme 3.i. To assess the involvement of 5-decyne in the formation of aromatic compounds 4, two additional experiments were performed: one using 5-decyne and one with a mixture of 1-hexyne/5decyne (4/1 v/v ratio). The first reaction with 5-decyne gave only traces of 3a and 3b (<1% molar conversion), confirming

Scheme 3. Proposed Mechanism for the Formation of (i) 5-Decyne from 1-Hexyne and (ii) 1-Hexyne from 5-Decyne



that an initial alkyne metathesis produced 1-hexyne, which after cyclotrimerization give the aromatic products **3** (Scheme 3ii). The catalytic run with a mixture of 1-hexyne/5-decyne gave the same products as with the 1-hexyne experiment: tri- and tetrasubstituted benzene derivatives **3** and **4**. Nevertheless, the tetrasubstituted product represents more than 13% of the overall products in comparison to 1.5% when using only 1-hexyne. This result strongly supports that the cross-alkyne cyclization between 1-hexyne and 5-decyne is taking place, leading to the two observed products **4**.

Since both precursors 1 and 2 produce similar results for the 1-hexyne cyclotrimerization, we chose to employ 1 to examine other terminal alkynes (Table 1).

Table 1. Alkyne Cyclotrimerization using	ble 1. Alkvne	Cvclotrime	erization	using 1	a
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entry	substrate <sup>b</sup>	conversion (%)	TON <sup>c</sup>	benzene product $(a/b)^d$
1	1-hexyne	99	5769	3 (29/71)
2	1-heptyne	99	5043	5 (31/69)
3	1-octyne	99	4501	6 (30/70)
4	1-decyne	98	3646	7 (31/69)
5	5-methylhex-1-yne	99	4994	8 (32/68)
6	cyclohexylethyne	81	1530	9 (59/41)
7	1-hexyne (1 mL)	95	11116	3
8	1-hexyne (2 mL)	55	12883	3

<sup>*a*</sup>Conditions: 1, 25 mg (0.75  $\mu$ mol of W); molar ratio alkyne/tungsten 3800–5900; 150 °C. <sup>*b*</sup>A 0.5 mL portion of substrate was used, except for entries 7 and 8. <sup>*c*</sup>TON is expressed in mol of alkyne transformed/mol of W. <sup>*d*</sup>The ratio of the regioisomers (1,3,5- and 1,2,4-trisubstituted benzene) was determined by GC analysis.

Under these reaction conditions, terminal alkynes were converted to the corresponding benzene derivatives in very high conversions (>98%) with TONs of 3646-5769 (entries 1-5). Replacing the aliphatic chain with cyclohexyl afforded the corresponding trimerized products, albeit in lower TON due to probably the steric hindrance of the cyclohexyl moiety (entry 6). With regard to the selectivity, the 1,2,4-trimer is the major product in most cases (entries 1-5), except with the cyclohexyl substrate, where a ratio of 59/41 was obtained (entry 6). To account for such regioselectivity, this cyclotrimerization reaction likely involves the formation of different metal-lacyclopentadiene isomers. Finally, increasing the 1-hexyne/W ratio gave the maximum TONs of 12000 (entries 7 and 8).

Next, the conversion of 1-octyne versus time was monitored by GC. After only 7 h, 1-octyne is mostly converted into aromatic products (>99%) (Figure 1). These supported W surface species were found to be highly active precursor catalysts for the 1-octyne cyclotrimerization with an initial TOF of 1.03 s<sup>-1</sup> (measured at 15 min). One advantage of such system in comparison to the reported WO<sub>3</sub>/SiO<sub>2</sub> is the lower temperature of the reaction (150 °C vs >250 °C).

In this supported catalytic system, we assume that these W species have a "single-site" character. Knowing the propensity of these W methylidyne/methyl species to form bimetallic species in solution,<sup>14</sup> we also studied the imaging characterization of oxidized supported  $\equiv$ Si $-O-WMe_5$  to determine the distribution of the W atom on the surface by scanning transmission electron microscopy (STEM) with spherical aberration correction. The microscope was operated at an accelerating voltage of 300 keV, offering a high enough spacial resolution for atomic high-angle annular dark-field imaging



**Figure 1.** Cyclotrimerization of 1-octyne catalyzed by **1**. Experimental conditions: **1** (25 mg, 0.75  $\mu$ mol, W loading 0.55 wt %, 1 equiv), 1-octyne (3.38 mmol, 4500 equiv), 150 °C, batch reactor.

(HAADF), which is convenient to discriminate heavy-element atoms such as W. Since our complex is highly air-sensitive, a pressure of dry oxygen (1 atm) was introduced in a batch reactor and maintained for 10 min prior to analysis. With a high ratio C/W of the resulting powder, we also did a plasma oxygen cleaning to prevent the formation of carbon during the analysis. Figure 2a shows the atomic resolution HAADF image of



Figure 2. (a) HAADF STEM image and (b) HAADF intensity profile of oxidized species 1.

discrete single W atoms on the surface of silica. The bright spots correspond to single W atoms, since HAADF is a Z contrast imaging method. Figure 2b represents the HAADF intensity profile along the line imposed on Figure 2a. The dispersed peaks indicate that the heavy W atoms with large atom number Z = 74 and demonstrate a full width at halfmaximum (fwhm) of 0.135 nm, close to the W atom radius (0.141 nm). Therefore, single W atoms of oxidized species 1 were observed, supporting the notion that immobilized W atoms are well dispersed after the grafting of initial tungsten hexamethyl upon silica.<sup>15</sup>

Overall, the above results show that single-site species 1 and 2 efficiently catalyze terminal alkyne cyclotrimerization rather than the classical alkyne metathesis.<sup>16</sup> Moreover, the alkyne substrate, which could act as a four-electron donor  $(\sigma + \pi)$ , does not prevent the cyclotrimerization reaction, as is known with tris(alkyne) tungsten 18-electron complexes.<sup>17</sup> This raises the question of the origin of such reactivity. DFT calculations were performed to elucidate the matter. We chose propyne as a substrate to avoid the complication of the conformational flexibility of the saturated  $n-C_6$  tail of 1-octyne. The process starts with the W-carbyne bipodal species 2, followed by coordination of the first propyne to form the tungstenacyclobutadiene derivative 10. The well-known loss of a proton from this metallacycle to the methyl group bound to W, releasing a methane molecule,18 is not favored in our case, since it is predicted to have a barrier of 69.7 kcal/mol. This is in agreement with the fact that no polymeric product is observed, since deprotonation of the metallacyclobutadiene would lead to a polymerization process.<sup>19</sup> Rather, the further insertion of an alkyne molecule to give the WVI-cyclohexatriene 11 is less demanding, with a  $\Delta G^{\ddagger}$  value of 16.8 kcal/mol, and is strongly exergonic, with an energy gain of 41.1 kcal/mol. Next, the  $W^{V_1}$ species 11 is reduced by overcoming a barrier of 11.8 kcal/mol to produce the bis-methylcyclopentadienyl W<sup>IV</sup> species 12, with an energy gain of 19.7 kcal/mol. This metallocene derivative precedes the third insertion, which starts with the easy alkyne coordination to the W center of 13, by overcoming a low barrier of 7.7 kcal/mol. Intermediate 13 evolves into 14 through formation of a C-C bond between the coordinated alkyne and a substituted C atom of the five-carbon ring. Although this step involves a significant barrier of 31.4 kcal/ mol, the alternative methane formation due to the interaction of the methyl group bonded to W and the nearest H atom of the five-membered ring costs 60.7 kcal/mol. Intermediate 14 evolves first to the bicyclo intermediate 15 and then to intermediate 16, presenting a seven-carbon ring and overcoming the high barrier of 29.6 kcal/mol. However, the formation of 16 is thermodynamically highly favored, by 30.5 kcal/mol, and this high stability of 16 can be also related to the next barrier of 35.0 kcal/mol to give species 17, which presents the final six-membered carbon ring. This step is considered as the rate-determining step of the reaction pathway. Finally the assistance of a fourth alkyne insertion leads to intermediate 17, overcoming a barrier of just 13.0 kcal/mol and facilitating the next release of the 1,2,4-methylbenzene. For this final step to regenerate the propagative species 10 to close the catalytic cycle, a 2 + 2 cycloreversion to release the trisubstituted benzene product overcomes the last barrier of 17.7 kcal/mol.

To switch to the alternative formation of a 1,3,5trisubstituted benzene derivative, from species **15** a barrier 3.2 kcal/mol higher leads to the isomer **16**' with a symmetric 1,3,5-methyl substitution. The next steps are identical with those in the formation of the unsymmetrical product.

On the other hand, the opposite regiochemistry of addition of propyne to the W-carbyne species 2, leading to the metallacycle 10'', was examined in Scheme S1 (Supporting Information). Formation of 10'' costs only 2.1 kcal/mol more than formation of 10. However, the 1,2,4-trisubstituted benzene formation is favored energetically as well. The formation of the metallocene intermediate 12 is in competition with an alkyne Scheme 4. Proposed Mechanism for the Formation of 1,2,4- and 1,3,5-Trisubstituted Benzene Derivatives<sup>a</sup>



<sup>a</sup>Energies are given in kcal/mol; carbon atoms are labeled in green.

insertion (see Scheme S2 (Supporting Information)). Indeed, this third insertion has two steps, consisting of a classic alkyne metathesis step leading to intermediate 18, with an energy barrier of 28.7 kcal/mol, followed by a rearrangement of the carbon skeleton to intermediate 19, with an energy barrier of 17.3 kcal/mol and an overall energy gain of 17.4 kcal/mol. This step can be seen as a Cope-like reaction, with the C=C double bond of the metallacyclobutane acting as the olefin. Interestingly, the final intermediate 19 has a structure consistent with a metallacyclopentene, with two W-C  $\sigma$ bonds (W-C3 and W-C7) and with the sequence of bond lengths C3–C2 = 1.44 Å, C2–C1 = 1.41 Å, and C1–C7 = 1.44 Å, which is a long-short-long rather than a short-long-short sequence, which would have been consistent with a  $\eta^4$ coordinated diene geometry. A final fourth insertion step of a propyne unit leads to intermediate 20, from which the 1,2,4trisubstituted benzene product is eliminated via an energy barrier of 27.8 kcal/mol, closing the catalytic cycle through recovery of the tungstenacyclobutene intermediate 10. Interestingly, intermediate 20 presents two clear  $\sigma$  bonds, W-C2 = 2.22 Å and C5-C6 = 1.54 Å, and two C-C double bonds, C1–C7 = 1.38 Å and C3–C4 = 1.36 Å.

Bearing in mind that the consecutive insertion of alkyne molecules in Schemes 4 and Schemes S1-S3 (Supporting Information) is consistent with the low steric hindrance of these systems, this alternative mechanism favoring the third alkyne insertion instead of the formation of the five-carbon ring in species 12 cannot be excluded. Indeed, species 12 could be a stalemate in such an alternative mechanism. This consecutive alkyne insertion explains why the use of bulky alkoxide groups

is generally required in the coordination sphere of the W metal to favor the alkyne metathesis.<sup>20</sup> Finally the alkyne addition step **10** to **11** was compared with release of acetylene from **10**, through a classic alkyne metathesis step. We found the latter to be disfavored by 9.7 kcal/mol, explaining why alkyne cyclotrimerization is favored over alkyne metathesis under our reaction conditions.

As final remark, we note that in many cases we did not investigate the regiochemistry of alkyne reactivity or other types of skeletal rearrangements. However, the number of possibilities to explore is practically infinite, which makes it impossible to investigate all of them in detail. Nevertheless, we believe that the overall catalytic cycle shown in Scheme 4 captures well the complex transformations promoted by this supported W catalyst, offering a sound rationalization of the experimental results.

#### CONCLUSION

We reported an efficient cyclotrimerization of terminal alkynes. In addition, DFT calculations show why this chemical transformation is favored instead of the typical alkyne metathesis. This study clearly highlights the importance of the coordination sphere of the W metallacyclobutadiene which is detrimental for alkyne metathesis.

## EXPERIMENTAL SECTION

All experiments were conducted under an argon atmosphere using glovebox techniques. The syntheses and the treatments of the surface species were carried out using high-vacuum lines ( $<10^{-5}$  mbar) and glovebox techniques. Pentane and dichloromethane were distilled

respectively from Na and CaH<sub>2</sub>. Elemental analyses were performed at the London Metropolitan University in London, U.K., and Mikroanalytisches Labor Pascher in Remagen, Germany. Terminal alkynes were purchased from Aldrich, distilled, degassed via several freeze-pump-thaw cycles, filtered over activated alumina, and stored under nitrogen. The supported precatalyst  $[(\equiv SiO)WMe_5]$  (1) and W methylidyne/methyl species 2 were prepared according to the literature. GC measurements were performed with an Agilent 7890A Series instrument (FID detection). Method for GC analyses: column HP-5; 30 m length  $\times$  0.32 mm i.d.  $\times$  0.25  $\mu$ m film thickness; flow rate 1 mL/min  $(N_2)$ ; split ratio 50/1; Inlet temperature 250 °C; detector temperature 250 °C. GC-MS measurements were performed with an Agilent 7890A Series instrument coupled with an Agilent 5975C Series instrument. The GC/MS instrument equipped with a capillary column coated with nonpolar stationary phase HP-5MS was used for molecular weight determination and identification, which allowed the separation of hydrocarbons according to their boiling point differences. The microscope (FEI Titan 80) was operated at an accelerating voltage of 300 kV, offering a high enough spatial resolution for atomic high-angle annular dark-field (HAADF) imaging, which is convenient to discriminate heavy-element atoms such as W.

General Procedure for Alkyne Cyclotrimerization. All reactions were carried out following the same protocol: a flamedried ampule was filled with the catalyst (25 mg, 0.75  $\mu$ mol, W loading: 0.55 wt %) in a glovebox, and the terminal alkyne (0.5 mL) was then added. The ampule was sealed under vacuum, immersed in an oil bath, and heated to 150 °C. At the end of the reaction, the ampule was cooled to -78 °C. Then, the mixture was diluted by addition of the external standard n-pentane and after filtration the resulting solution was analyzed by GC and GC/MS. For the kinetic studies on 1-octyne cyclotrimerization, each analysis represents an independent run.

1,3,5-Tributylbenzene/1,2,4-Tributylbenzene (3a/3b). Yellow oil. IR (thin film): 2961, 2922, 2856, 1460, 1375, 821, 703 cm<sup>-1</sup>. <sup>1</sup>H NMR  $\delta_{\rm H}$  (CDCl<sub>3</sub>, 600 MHz): 7.05 (d, 1H,  ${}^{3}J_{\rm HH}$  = 7.5 Hz, Ar), 6.95–6.93 (m, 2H, Ar), 6.82 (s, 3H, Ar), 2.59-2.53 (m, ArCH<sub>2</sub>C), 1.59-1.54 (m, CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 1.41-1.34 (m, CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 0.97-0.91 (m, CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>). <sup>13</sup>C NMR δ<sub>C</sub> (CDCl<sub>3</sub>, 150 MHz): 142.8, 140.4, 140.2, 137.8, 129.4, 129.1, 126.0, 125.8, 35.8, 35.4, 33.9, 33.7, 32.6, 32.1, 23.0, 22.6, 14.1. MS (EI): m/z 246. 3a/3b = 29/71, determined by GC analysis. HRMS: calcd for  $C_{18}H_{30}$  (M)<sup>+</sup> 246.23420, found (M)<sup>+</sup> 246.23360. Anal. Calcd for C18H30: C, 87.73; H, 12.27. Found: C, 87.60; H, 12.16 (measured using a mixture of isomers).

1,3,5-Tripentylbenzene/1,2,4-Tripentylbenzene (5a/5b). Yellow oil.<sup>21</sup> IR (thin film): 2951, 2923, 2853, 1454, 1376, 824, 726, 703 cm<sup>-1</sup>. <sup>1</sup>H NMR  $\delta_{\rm H}$  (CDCl<sub>3</sub>, 400 MHz): 7.05 (d, 1H, <sup>3</sup>J<sub>HH</sub> = 7.5 Hz, Ar), 6.95-6.93 (m, 2H, Ar), 6.82 (s, 3H, Ar), 2.59-2.53 (m, ArCH<sub>2</sub>C), 1.62–1.56 (m, CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 1.37–1.32 (m, CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 0.92–0.88 (m, CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>). <sup>13</sup>C NMR  $\delta_{\rm C}$  (CDCl<sub>3</sub>) 100 MHz): 142.8, 140.5, 140.3, 137.8, 129.4, 129.1, 126.0, 125.8, 36.1, 35.7, 32.9, 32.4, 32.2, 31.8, 31.4, 31.2, 22.7, 14.2. 5a/5b = 31/69, determined by GC analysis. MS (EI): m/z 288. HRMS: calcd for C21H36 (M)+ 288.28115, found (M)+, 288.28008. Anal. Calcd for C21H36: C, 87.42; H, 12.58. Found: C, 87.47; H, 12.38 (measured using a mixture of isomers).

1,3,5-Trihexylbenzene/1,2,4-Trihexylbenzene (6a/6b). Yellow oil.<sup>21</sup> IR (thin film): 2948, 2917, 2847, 1451, 1375, 824, 719 cm<sup>-1</sup>. <sup>1</sup>H NMR  $\delta_{\rm H}$  (CDCl<sub>3</sub>, 600 MHz): 7.05 (d, 1H, <sup>3</sup> $J_{\rm HH}$  = 7.5 Hz, Ar), 6.95-6.93 (m, 2H, Ar), 6.81 (s, 3H, Ar), 2.60-2.54 (m, ArCH<sub>2</sub>C), 1.62-1.55 (m, CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 1.38-1.32 (m, CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 0.91-0.89 (m,  $CH_2CH_2CH_3$ ). <sup>13</sup>C NMR  $\delta_C$  (CDCl<sub>3</sub>, 150 MHz): 142.8, 140.5, 140.3, 137.8, 129.4, 129.1, 126.0, 125.8, 36.1, 35.7, 32.9, 32.5, 31.9, 31.7, 31.5, 29.7, 29.3, 22.8, 14.2. 6a/6b = 30/70, determined by GC analysis. MS (EI): m/z 330. HRMS: calcd for  $C_{24}H_{42}$  (M)<sup>+</sup> 330.32810, found (M)<sup>+</sup> 330.32683. Anal. Calcd for C<sub>24</sub>H<sub>42</sub>: C, 87.19; H, 12.81. Found: C, 87.29; H, 12.88 (measured using a mixture of isomers).

1,3,5-Trioctylbenzene/1,2,4-Trioctylbenzene (7a/7b). Yellow oil.<sup>22</sup> IR (thin film): 2951, 2917, 2844, 1454, 1378, 817, 716 cm<sup>-1</sup>. <sup>1</sup>H NMR  $\delta_{\rm H}$  (CDCl<sub>3</sub>, 400 MHz): 7.05 (d, 1H,  ${}^{3}J_{\rm HH}$  = 7.5 Hz, Ar), 6.95–6.93

(m, 2H, Ar), 6.81 (s, 3H, Ar), 2.57–2.53 (m, ArCH<sub>2</sub>C), 1.60–1.56 (m,  $CH_2CH_2CH_3$ ), 1.28 (m,  $CH_2CH_2CH_3$ ), 0.91–0.89 (m,  $CH_2CH_2CH_3$ ). <sup>13</sup>C NMR  $\delta_C$  (CDCl<sub>3</sub>, 100 MHz): 142.8, 140.5, 140.3, 137.8, 129.4, 129.1, 126.0, 125.8, 36.1, 35.7, 32.9, 32.5, 32.1, 31.8, 31.6, 30.0, 29.7, 29.6, 29.4, 22.8, 14.2. 7a/7b = 31/69, determined by GC analysis. MS (EI): m/z 414. HRMS: calcd for C30H54 (M)+ 414.42200, found (M)+ 414.42053. Anal. Calcd for C<sub>30</sub>H<sub>54</sub>: C, 86.88; H, 13.12. Found: C, 86.81; H, 13.28 (measured using a mixture of isomers).

1,3,5-Triisopentylbenzene/1,2,4-Triisopentylbenzene (8a/8b). Yellow oil. IR (thin film): 2948, 2926, 2860, 1467, 1384, 1365, 1166, 811, 824, 703 cm<sup>-1</sup>. <sup>1</sup>H NMR  $\delta_{\rm H}$  (CDCl<sub>3</sub>, 600 MHz): 7.04 (d, 1H, <sup>3</sup>J<sub>HH</sub> = 7.5 Hz, Ar), 6.95-6.93 (m, 2H, Ar), 6.82 (s, 3H, Ar), 2.58-2.54 (m, ArCH<sub>2</sub>C), 1.66–1.58 (m, CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 1.52–1.43 (m, CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 0.98–0.90 (m, CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>). <sup>13</sup>C NMR  $\delta_{\rm C}$  (CDCl<sub>3</sub>, 150 MHz): 143.1, 140.7, 140.5, 137.9, 129.3, 129.2, 125.8, 41.1, 41.0, 34.0, 33.5, 30.8, 30.3, 28.6, 28.5, 28.0, 22.7. 8a/8b = 32/68, determined by GC analysis. MS (EI): m/z 288. HRMS: calcd for  $C_{21}H_{36}\ (M)^{*}$  288.28115, found  $(M)^{*},$  288.28000. Anal. Calcd for C21H36: C, 87.42; H, 12.58. Found: C, 87.35; H, 12.45 (measured using a mixture of isomers).

1,3,5-Tricyclohexylbenzene/1,2,4-Tricyclohexylbenzene (9a/9b). Colorless oil. IR (thin film): 2923, 2847, 1450, 907, 724 cm<sup>-1</sup>. <sup>1</sup>H NMR  $\delta_{\rm H}$  (CDCl<sub>3</sub>, 600 MHz): 7.14 (d, 1H,  ${}^{3}J_{\rm HH}$  = 8.0 Hz, Ar), 7.0 (app s, 1H, Ar), 7.0-6.99 (m, 1H, Ar), 6.88 (s, 3H, Ar), 2.79-2.74 (m, ArCHC), 2.46 (app s, ArCHC), 1.90-1.73 (m, CH<sub>2</sub>), 1.46-1.37 (m, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 1.29–1.24 (m, CH<sub>2</sub>). <sup>13</sup>C NMR  $\delta_{\rm C}$  (CDCl<sub>3</sub>, 150 MHz): 147.9, 145.1, 144.6, 142.1, 125.7, 124.6, 124.0, 123.0, 44.9, 44.4, 39.4, 39.1, 34.9, 34.8, 34.7, 34.6, 34.6, 27.4, 27.1, 26.5, 26.4. 9a/ 9b = 59/41, determined by GC analysis. MS (EI): m/z 324. HRMS: calcd for  $C_{24}H_{36}$  (M)<sup>+</sup> 324.28115, found: (M)<sup>+</sup>, 324.28042. Anal. Calcd for C24H36: C, 88.82; H, 11.18. Found: C, 88.72; H, 11.29 (measured using a mixture of isomers).

Computational Details. All DFT static calculations were performed at the GGA level with the Gaussian09 set of programs using the BP86 functional of Becke and Perdew.<sup>23</sup> The electronic configuration of the molecular systems was described with the standard split-valence basis set with a polarization function of Ahlrichs and co-workers for H, C, Si, and O (SVP keyword in Gaussian).<sup>24</sup> For W, we used the small-core, quasi-relativistic Stuttgart/Dresden effective core potential, with an associated valence basis set contracted (standard SDD keywords in Gaussian 09).<sup>25</sup> A cluster of  $Si_2O_4H_4W$ units was chosen, and no symmetry constraints were imposed in any case. The stationary points were identified exactly by the curvature of the potential-energy surface at these points corresponding to the eigenvalues of the Hessian. All reported transition states possess exactly one negative Hessian eigenvalue, while all other stationary points exhibit exclusively positive eigenvalues. It should be noted that the entropic contribution calculated in the gas phase (p = 1 atm) is likely exaggerated in dissociative steps.<sup>26</sup> All thermochemical analyses were performed at p = 1354 atm, as suggested by Martin et al.<sup>2</sup>

The reported energies have been optimized via single-point calculations on the BP86 geometries ( $\Delta G^{\circ}$  at 150 °C) with triple- $\zeta$ valence plus polarization (TZVP keyword in Gaussian) using the M06 functional; however, solvent effects were estimated with the polarizable continuous solvation model PCM using DCM as solvent.

#### ASSOCIATED CONTENT

#### Supporting Information

Figures and tables giving IR, NMR, and other characterization data and calculation details. This material is available free of charge via the Internet at http://pubs.acs.org.

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#### Notes

The authors declare no competing financial interest.

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