


Cite this: *RSC Adv.*, 2021, **11**, 39518

Received 11th November 2021  
Accepted 15th November 2021

DOI: 10.1039/d1ra08268j

rsc.li/rsc-advances

# Cp<sub>2</sub>ZrCl<sub>2</sub> – Et<sub>3</sub>Al reagent system in the homo-coupling of trimethylsilyl-substituted alkynes†

Ilfir R. Ramazanov,\* Rita N. Kadikova,  Aliya K. Amirova, Oleg S. Mozgovoij and Usein M. Dzhemilev

The reaction of trimethylsilyl-substituted alkynes with 0.5 equivalents of Cp<sub>2</sub>ZrCl<sub>2</sub> and 1 equivalent of Et<sub>3</sub>Al in toluene at room temperature for 18 hours gives, after hydrolysis/deuterolysis or iodination, functionalized products of the homo-coupling of silyl-substituted alkynes in good yield. Trimethylsilyl-substituted  $\alpha,\omega$ -diynes react with the Cp<sub>2</sub>ZrCl<sub>2</sub> – Et<sub>3</sub>Al reagent system to give (1*Z*,2*Z*)-1,2-bis(iodo(trimethylsilyl)methylene)cycloalkanes after iodinolysis.

## 1 Introduction

The reaction of homo-coupling of alkynes using zirconocene reagents is an important basis for the efficient synthesis of polymers, oligomers and macrocycles.<sup>1</sup> It is generally accepted that the transformation takes place through the intermediate formation of “Cp<sub>2</sub>Zr” species that can be generated by the interaction of Cp<sub>2</sub>ZrCl<sub>2</sub> with alkali and alkaline earth metals, as well as with alkyl derivatives of metals. The most widely used reagents include the Negishi reagent (“Cp<sub>2</sub>ZrBu<sub>2</sub>”),<sup>2,3</sup> Takahashi reagent (“Cp<sub>2</sub>ZrEt<sub>2</sub>”),<sup>4</sup> and Rosenthal reagent (Cp<sub>2</sub>Zr(py)TMSC≡CTMS).<sup>5–7</sup> Despite detailed studies of the reaction of Et<sub>3</sub>Al with Cp<sub>2</sub>ZrCl<sub>2</sub>,<sup>8–12</sup> the resulting zirconocene complexes could not be successfully used for intramolecular coupling of alkynes. Negishi has demonstrated that the reaction of diphenylacetylene with Et<sub>3</sub>Al in the presence of 10 mol% of Cp<sub>2</sub>ZrCl<sub>2</sub> in benzene at 55 °C gave a mixture of substituted alkene and diene in a 1 : 1 ratio with a total yield of 90%.<sup>13</sup> However, the reaction with 5-decyne under similar conditions resulted in the formation of only 5-ethyl-5-decene. By replacing Et<sub>3</sub>Al with Pr<sub>3</sub>Al, it was possible to convert 5-decyne into tetrasubstituted 1,3-diene in 38% yield with simultaneous formation of reduction products in the amount of 63%.<sup>14</sup> Thus, attempts to develop a synthetically useful methodology for the coupling of alkynes using trialkylaluminums and Cp<sub>2</sub>ZrCl<sub>2</sub> were unsuccessful. However, from our early observations of the alkyne cycloalumination reaction with Et<sub>3</sub>Al in the presence of catalytic amounts of Cp<sub>2</sub>ZrCl<sub>2</sub>, we noticed that trimethylsilyl substituted 1-hexyne under the reaction conditions gave 1,4-diene hydrocarbons as a by-product in up to 20% yield. This gave hope for the possibility of selecting the optimal conditions for the

implementation of the homo-coupling reaction of silicon containing alkynes. The importance of this transformation was due to the possibility of its use for the preparation of macrocyclic zirconacyclopentadiene compounds through the combination of diyne molecules of the TMS-C≡C-R-C≡C-TMS type.

## 2 Results and discussion

It was found that the reaction of silyl-substituted alkynes with 1 equivalent of Cp<sub>2</sub>ZrCl<sub>2</sub> and 2 equivalents of Et<sub>3</sub>Al in toluene at 23 °C for 18 hours after hydrolysis/deuterolysis or iodinolysis gives homo-coupling products 2–4 in good yield (Table 1). A remarkable feature of the reaction is the complete absence of products of cyclic carbometallation 5. In the case of 1-alkyl-2-(trimethylsilyl)acetylenes, the reaction proceeds with a high regioselectivity to give 3,4-dialkyl substituted 1,4-bis(trimethylsilyl)buta-1,3-diene. However, the reaction with trimethyl(phenylethynyl)silane under similar conditions gives a mixture ((1*E*,3*E*)-2,3-diphenylbuta-1,3-diene-1,4-diyl) bis(trimethylsilane) 2e and ((1*E*,3*Z*)-2,4-diphenylbuta-1,3-diene-1,3-diyl)bis(trimethylsilane) 2e' in a 5 : 1 ratio. The reaction of trimethylsilyl-substituted  $\alpha,\omega$ -diynes (1,7-octadiyne, 1,8-nonadiyne) with Cp<sub>2</sub>ZrCl<sub>2</sub> – Et<sub>3</sub>Al reagent system after iodinolysis gives (1*Z*,2*Z*)-1,2-bis(iodo(trimethylsilyl)methylene)cycloalkanes 6 and 7 in good yield (Scheme 1). We were unable to obtain the products of the homo-coupling of alkynes in the case of 5-decyne and hex-1-yn-1-ylbenzene. As a result of the reaction, these alkynes gave after deuterolysis only products of cyclic carbometallation 5f and 5g. We failed to involve in the reaction acetylene derivatives of more sterically hindered silanes: hex-1-yn-1-yltriisopropylsilane, *tert*-butyl(hex-1-yn-1-yl)dimethylsilane and 1,2-bis(trimethylsilyl)ethyne. The above-mentioned acetylenic compounds were inert under the reaction conditions.

The solvent has a significant effect on the reaction. When replacing toluene with hexane, in the case of a reaction with hept-1-yn-1-yltrimethylsilane, we obtained after deuterolysis the

Institute of Petrochemistry and Catalysis of Russian Academy of Sciences, 141 Prospekt Oktyabrya, Ufa 450075, Russian Federation. E-mail: ilfir.ramazanov@gmail.com

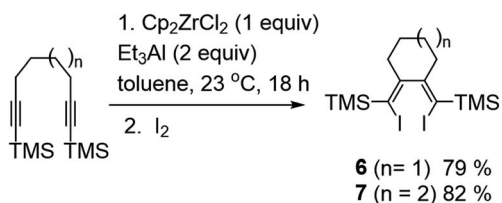
† Electronic supplementary information (ESI) available. See DOI: 10.1039/d1ra08268j



**Table 1** The homo-coupling of silyl-substituted alkynes by  $\text{Cp}_2\text{ZrCl}_2$  –  $\text{Et}_3\text{Al}$  reagent

$\text{R} \equiv \text{R}' \xrightarrow[\text{2. H}_2\text{O or D}_2\text{O or I}_2]{\text{1. Cp}_2\text{ZrCl}_2 \text{ (0.5 equiv)} \\ \text{Et}_3\text{Al (1 equiv)} \\ \text{toluene, 23 }^\circ\text{C, 18 h}}$			$\begin{array}{cc} \text{R} & \text{R}' \\   &   \\ \text{X} & \text{X} \end{array} + \begin{array}{c} \text{R} & \text{R}' \\   &   \\ \text{X} & \text{X} \end{array}$	
a: R = Bu; R' = TMS	2 (X = H)	5 (X = D)		
b: R = Am; R' = TMS	3 (X = D)			
c: R = Hex; R' = TMS	4 (X = I)			
d: R = Oct; R' = TMS				
e: R = Ph; R' = TMS				
g: R = Bu; R' = Bu				
h: R = Bu; R' = Ph				

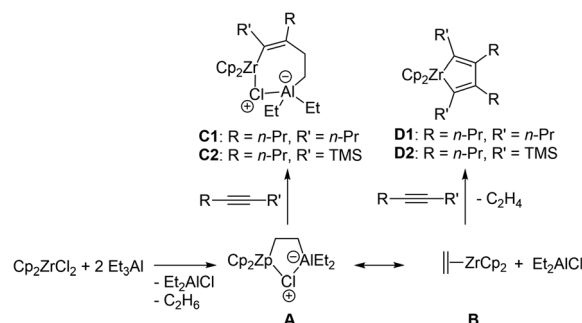
Entry	R	R'	X		
1	Bu	TMS	H	86% (2a)	nd
2	Bu	TMS	I	88% (4a)	nd
3	Am	TMS	H	83% (2b)	nd
4	Am	TMS	D	85% (3b)	nd
5	Am	TMS	I	69% (4b)	nd
6	Hex	TMS	H	78% (2c)	nd
7	Oct	TMS	H	84% (2d)	nd
8	Oct	TMS	I	69% (4d)	nd
9	Ph	TMS	H	61% (2e) + 12% (2e')	nd
10	Bu	Bu	D	nd	82% (5f)
11	Bu	Ph	D	nd	69% (5g)

**Scheme 1** The reaction of trimethylsilyl-substituted  $\alpha,\omega$ -diynes with  $\text{Cp}_2\text{ZrCl}_2$  –  $\text{Et}_3\text{Al}$  reagent system.

mixture of the compound **3b** in 60% yield with the product of cyclic carbometallation **5b** in 20% yield. In diethyl ether and diisopropyl ether, the reaction does not take place.

We assume that the reaction proceeds through the stage of intermediate formation of the metallocyclopentadiene, which can be of a zirconocene or organoaluminum nature. The formation of a non-cyclic bimetallic intermediate is not excluded. Due to the high reactivity of organoaluminum compounds in the reaction mixture with respect to oxygen, the isolation and identification of this metallocyclopentadiene is difficult. Scheme 2 depicts the proposed mechanism for the formation of zirconacyclopentadienes and zirconacyclopentenes under the reaction conditions. Intermediate **A**, formed by mixing 1 equivalent of  $\text{Cp}_2\text{ZrCl}_2$  and 2 equivalents of  $\text{Et}_3\text{Al}$ , was previously well characterized.<sup>5–9</sup>

Scheme 2 depicts the proposed mechanism of the reaction. Intermediate **A**, formed by mixing 1 equivalent of  $\text{Cp}_2\text{ZrCl}_2$  and

**Scheme 2** The proposed mechanism of the formation of zirconacyclopentadienes.

2 equivalents of  $\text{Et}_3\text{Al}$ , was previously well characterized.<sup>8–12</sup> The further reaction of intermediate **A** with dialkyl substituted alkynes proceeds as an alkyne insertion as it was describes by Negishi.<sup>13</sup> It can be assumed that the insertion of trialkylsilyl-substituted acetylenes is more difficult, since the rate of cycloaluminum of trialkylsilyl-substituted acetylenes is lower compared to dialkyl-substituted acetylenes.<sup>14</sup> According to quantum chemical calculations at B3LYP/6-31G\*/LANL2DZ level of theory in gas phase, the standard Gibbs energy of the insertion reaction is lower in the case of 4-octyne (**A** → **C1**) by 11.6 kcal mol<sup>−1</sup> compared to the insertion of trimethyl(pent-1-yn-1-yl)silane (**A** → **C2**). At the same time, according to the calculations, the formation of zirconacyclopentadiene **D** from intermediate **A** is thermodynamically more efficient process in the case of 4-octyne (**A** → **D1**) rather than trimethyl(pent-1-yn-1-yl)silane (**A** → **D2**). The standard Gibbs energies of the corresponding hypothetical reactions are −9.4 and 8.9 kcal mol<sup>−1</sup>, respectively. Thus, there are no kinetic or thermodynamic grounds for the predominant formation of metalacyclopentadiene intermediates in the case of trimethylsilyl-substituted acetylenes. Then we assumed that there is an equilibrium between intermediate **A** and zirconocene–ethylene complex **B**. We have already postulated the existence of such an equilibrium in the cycloaluminum of 1-alkynylphosphines<sup>15</sup> and olefins.<sup>16</sup> The reaction of alkynes with intermediate **B** can be responsible for the formation of zirconacyclopentadiene intermediates. The following hypothesis was proposed to explain experimental results: If alkyne is sufficiently reactive for the insertion into Zr–C bond of intermediate **A** then it will be consumed mainly for the formation of the product of cyclic carbometallation, or else alkyne will react with the zirconocene–ethylene complex to give homo-coupling product. In the case of trimethylsilyl-substituted acetylenes, bulky trimethylsilyl group hampers the insertion of alkyne into Zr–C bond of intermediate **A** and the formation of homo-coupling product is observed. However, when carrying out the reaction with hept-1-yn-1-yltrimethylsilane in hexane instead of toluene, we observed the side formation of the product of cyclic carbometallation **5b**, which should be formed as a result of the interaction of intermediate **A** with alkyne. This fact can also be explained within the framework of the proposed hypothesis. The point is that the use of a less polar solvent decreases the degree of solvation,



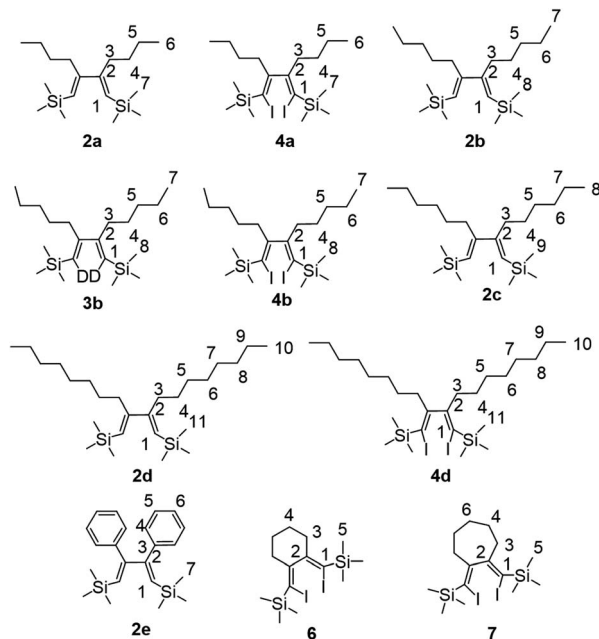


Fig. 1 The numbering of atoms in the reported  $^{13}\text{C}$ - and  $^1\text{H}$ -NMR spectral data of the compounds 2a-e, 3b, 4a, 4b, 4d, 6, 7.

increasing the effective charges of the atoms of the reaction center in intermediate **A**, which in turn increases the probability of the insertion of trimethylsilyl-substituted acetylene into the Zr-C bond to give the product of cyclic carbometallation after hydrolysis.

### 3 Conclusions

It was found that  $\text{Cp}_2\text{ZrCl}_2 - \text{Et}_3\text{Al}$  reagent system in toluene allows to prepare the products of the homo-coupling of silyl-substituted alkynes in good yield.

## 4 Experimental section

### 4.1. General data

The reagents were obtained from Sigma-Aldrich or Acros. Toluene was distilled over Na. Silyl-substituted alkynes were prepared by the reaction of terminal acetylenes with  $\text{EtMgBr}$  and trialkylchlorosilanes.<sup>17</sup> IR spectra were recorded on Bruker VE Vertex 70v spectrometer as liquid films or in Nujol and are reported in wavenumbers ( $\text{cm}^{-1}$ ). Nuclear magnetic resonance spectroscopy was performed on a Bruker Avance 500. The  $^1\text{H}$  NMR spectra were recorded at 500 MHz and  $^{13}\text{C}\{-^1\text{H}\}$  NMR spectra at 125 MHz in  $\text{CDCl}_3$ . The chemical shifts are reported in ppm relative to tetramethylsilane (TMS) as the internal standard. The numbering of atoms in the  $^{13}\text{C}$  and  $^1\text{H}$  NMR spectra of the compounds **2a-e**, **3b**, **4a**, **4b**, **4d**, **6**, **7** is shown in Fig. 1. Mass spectra were obtained on a Finnigan 4021 instrument. All quantum-chemical calculations were performed using B3LYP/6-31G(d)/LanL2DZ basis set as implemented in Gaussian 09 software.<sup>18</sup>

### 4.2. Homo-coupling of trimethylsilyl-substituted alkynes by $\text{Cp}_2\text{ZrCl}_2 - \text{Et}_3\text{Al}$ reagent

A suspension of  $\text{Cp}_2\text{ZrCl}_2$  (292 mg, 1.00 mmol) in toluene (3 mL) in a 25 mL round bottom flask was cooled with an ice-bath and then  $\text{Et}_3\text{Al}$  (0.3 mL, 2.00 mmol) was added. After stirring the mixture at  $0^\circ\text{C}$  for 30 minutes, 1 mmol of trimethylsilyl-substituted alkyne or 0.5 mmol of trimethylsilyl-substituted  $\alpha,\omega$ -diyne was added. The mixture was stirred at  $23^\circ\text{C}$  for 18 h. Then the mixture was diluted with hexane (5 mL) and  $\text{H}_2\text{O}$  (3 mL) (to prepare **2a-e**) or  $\text{D}_2\text{O}$  (3 mL) (to prepare **3b**) was added dropwise while cooling the reactor flask with an ice-bath. The precipitate was filtered on a filter paper. To prepare the compounds **4a**, **4b**, **4d**, a solution of  $\text{I}_2$  (787.5 mg, 6.25 mmol) in THF (5 mL) was added to the reaction mixture while cooling the reactor flask with an ice-bath and stirred at  $23^\circ\text{C}$  for 1 h. To prepare the compounds **6**, **7**, a solution of  $\text{I}_2$  (787.5 mg, 6.25 mmol) in THF (5 mL) was used. The aqueous layer was extracted with diethyl ether ( $3 \times 5$  mL). The combined organic layers were washed with brine (10 mL), dried over anhydrous  $\text{CaCl}_2$ . Evaporation of solvent and purification of the residue by column chromatography (hexane) gave a colourless oil.

#### 4.2.1. ((1*E*,3*E*)-2,3-Dibutylbuta-1,3-diene-1,4-diyl)

**bis(trimethylsilyl) (2a).**<sup>19</sup> Yield: 133 mg (86%);  $R_f = 0.8$  (hexane). IR (liquid film): 2956, 2873, 2861, 1593, 1561, 1465, 1248, 839, 769, 689, 619  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta = 0.14$  (s, 9H, C(7) $\text{H}_3$ ), 0.92 (t,  $J = 7.0$  Hz, 3H, C(6) $\text{H}_3$ ), 1.28–1.36 (m, 4H, C(4, 5) $\text{H}_2$ ), 2.29 (t,  $J = 6.4$  Hz, 2H, C(3) $\text{H}_2$ ), 5.48 (s, 1H, C(1)H).  $^{13}\text{C}\{-^1\text{H}\}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta = 0.36$  (C(7)), 14.06 (C(6)), 22.93 (C(5)), 31.69 (C(4)), 33.74 (C(3)), 125.07 (C(1)), 160.67 (C(2)).  $^{29}\text{Si}\{-^1\text{H}\}$  (500 MHz,  $\text{CDCl}_3$ ):  $-10.79$ . MS (EI):  $m/z$ , % = 311 (3) [ $\text{M}^+$ ], 295 (5), 268 (9), 237 (15), 207 (10), 165 (7), 138 (6), 73 (100), 45 (9).

**4.2.2. ((1*E*,3*Z*)-2,3-Dibutyl-1,4-diiodobuta-1,3-diene-1,4-diyl)bis(trimethylsilyl) (4a).**<sup>20</sup> Yield: 247 mg (88%);  $R_f = 0.6$  (hexane).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta = 0.36$  (s, 9H, C(7) $\text{H}_3$ ), 0.94 (t,  $J = 7.3$  Hz, 1H, C(6) $\text{H}_3$ ), 1.34 (q,  $J = 7.3$  Hz,  $J = 14.5$  Hz, 2H, C(5) $\text{H}_2$ ), 1.46–1.55 (m, 1H(A), 1H(B), C(4) $\text{H}_2$ ), 2.21 (t,  $J = 13.7$  Hz, 1H(A), C(3) $\text{H}_2$ ), 2.52 (t,  $J = 13.7$  Hz, 1H(B), C(3) $\text{H}_3$ ).  $^{13}\text{C}\{-^1\text{H}\}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta = 1.89$  (C(7)), 13.83 (C(6)), 23.26 (C(5)), 30.84 (C(4)), 36.25 (C(3)), 108.67 (C(1)), 163.54 (C(2)). MS (EI):  $m/z$ , % = 562 (<1) [ $\text{M}^+$ ], 435 (84), 185 (14), 161 (26), 139 (7), 73 (100), 45 (13).

#### 4.2.3. ((1*E*,3*E*)-2,3-Dipentylbuta-1,3-diene-1,4-diyl)

**bis(trimethylsilyl) (2b).** Yield: 141 mg (83%);  $R_f = 0.8$  (hexane). IR (liquid film): 2956, 2926, 2856, 1593, 1560, 1466, 1248, 839, 772, 689, 620  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta = 0.14$  (s, 9H, C(8) $\text{H}_3$ ), 0.91 (t,  $J = 7.0$  Hz, 3H, C(7) $\text{H}_3$ ), 1.28–1.35 (m, 6H, C(4, 5, 6) $\text{H}_2$ ), 2.29 (t,  $J = 6.0$  Hz, 2H, C(3) $\text{H}_2$ ), 5.48 (s, 1H, C(1)H).  $^{13}\text{C}\{-^1\text{H}\}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta = 0.35$  (C(8)), 14.03 (C(7)), 22.54 (C(6)), 29.13 (C(4)), 32.03 (C(5)), 33.95 (C(3)), 125.10 (C(1)), 160.69 (C(2)).  $^{29}\text{Si}\{-^1\text{H}\}$  (500 MHz,  $\text{CDCl}_3$ ):  $-10.82$ . MS (EI):  $m/z$ , % = 339 (4) [ $\text{M}^+$ ], 338 (11), 282 (15), 265 (30), 209 (8), 191 (10), 73 (100), 45 (8).  $\text{C}_{20}\text{H}_{40}\text{D}_2\text{Si}_2$  calc. C 70.92, H 12.50; CHN analysis, C 70.4, H 12.8.

#### 4.2.4. ((1*E*,3*E*)-2,3-Dipentylbuta-1,3-diene-1,4-diyl-1,4-d2)

**bis(trimethylsilyl) (3b).** Yield: 145 mg (85%);  $R_f = 0.8$  (hexane).



IR (liquid film): 2956, 2928, 2859, 1589, 1556, 1466, 1379, 1248, 1097, 1042, 837, 761, 689, 616  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 0.14 (s, 9H,  $\text{C}(8)\text{H}_3$ ), 0.91 (t,  $J$  = 6.7 Hz, 3H,  $\text{C}(7)\text{H}_3$ ), 1.28–1.33 (m, 6H,  $\text{C}(4, 5, 6)\text{H}_2$ ), 2.28 (t,  $J$  = 7.4 Hz, 2H,  $\text{C}(3)\text{H}_2$ ), 5.48 (s, 1H,  $\text{C}(1)\text{H}$ ).  $^{13}\text{C}$ - $\{^1\text{H}\}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 0.35 ( $\text{C}(8)$ ), 14.04 ( $\text{C}(7)$ ), 22.54 ( $\text{C}(6)$ ), 29.14 ( $\text{C}(4)$ ), 32.03 ( $\text{C}(5)$ ), 32.95 ( $\text{C}(3)$ ), 125.09 ( $\text{C}(1)$ ), 160.60 ( $\text{C}(2)$ ).  $^{29}\text{Si}$ - $\{^1\text{H}\}$  (500 MHz,  $\text{CDCl}_3$ ): –10.84. MS (EI):  $m/z$ , % = 341 (<1) [ $\text{M}^+$ ], 339 (4), 283 (5), 266 (10), 210 (4), 192 (5), 73 (100), 45 (6).  $\text{C}_{20}\text{H}_{42}\text{Si}_2$  calc. C 70.50; CHN analysis, C 70.1.

**4.2.5. ((1Z,3Z)-1,4-Diiodo-2,3-dipentylbuta-1,3-diene-1,4-diyl)bis(trimethylsilane) (4b).** Yield: 204 mg (69%);  $R_f$  = 0.7 (hexane). IR (liquid film): 2956, 2930, 2873, 1970, 1462, 1249, 1116, 841, 759, 693, 588  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 0.36 (s, 9H,  $\text{C}(8)\text{H}_3$ ), 0.92 (t,  $J$  = 7.1 Hz, 3H,  $\text{C}(7)\text{H}_3$ ), 1.28–1.31 (m, 2H,  $\text{C}(5)\text{H}_2$ ), 1.33–1.37 (m, 2H,  $\text{C}(6)\text{H}_2$ ), 1.50–1.56 (m, 1H(A),  $\text{C}(4)\text{H}_2$ ), 1.62–1.67 (m, 1H(B),  $\text{C}(4)\text{H}_2$ ), 2.22 (t,  $J$  = 13.2 Hz, 1H(A),  $\text{C}(3)\text{H}_2$ ), 2.50 (t,  $J$  = 13.3 Hz, 1H(B),  $\text{C}(3)\text{H}_2$ ).  $^{13}\text{C}$ - $\{^1\text{H}\}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 1.88 ( $\text{C}(8)$ ), 14.04 ( $\text{C}(7)$ ), 22.38 ( $\text{C}(6)$ ), 28.50 ( $\text{C}(4)$ ), 32.35 ( $\text{C}(5)$ ), 36.49 ( $\text{C}(3)$ ), 108.58 ( $\text{C}(1)$ ), 163.68 ( $\text{C}(2)$ ).  $^{29}\text{Si}$ - $\{^1\text{H}\}$  (500 MHz,  $\text{CDCl}_3$ ): 0.93. MS (EI):  $m/z$ , % = 591 (<1) [ $\text{M}^+$ ], 463 (13), 189 (10), 95 (3), 73 (100), 45 (4).  $\text{C}_{20}\text{H}_{40}\text{I}_2\text{Si}_2$  calc. C 40.68, H 6.83; CHN analysis, C 40.5, H 6.6.

**4.2.6. ((1E,3E)-2,3-Dihexylbuta-1,3-diene-1,4-diyl)bis(trimethylsilane) (2c).**<sup>19</sup> Yield: 143 mg (78%);  $R_f$  = 0.7 (hexane). IR (liquid film): 2956, 2927, 2857, 1592, 1561, 1466, 839, 771, 749, 689, 619  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 0.14 (s, 9H,  $\text{C}(9)\text{H}_3$ ), 0.91 (t,  $J$  = 6.9 Hz, 3H,  $\text{C}(8)\text{H}_3$ ), 1.28–1.33 (m, 8H,  $\text{C}(4, 5, 6, 7)\text{H}_2$ ), 2.29 (t,  $J$  = 7.3 Hz, 2H,  $\text{C}(3)\text{H}_2$ ), 5.48 (s, 1H,  $\text{C}(1)\text{H}$ ).  $^{13}\text{C}$ - $\{^1\text{H}\}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 0.35 ( $\text{C}(9)$ ), 14.06 ( $\text{C}(8)$ ), 22.59 ( $\text{C}(7)$ ), 29.40 ( $\text{C}(4)$ ), 29.47 ( $\text{C}(5)$ ), 31.73 ( $\text{C}(6)$ ), 34.00 ( $\text{C}(3)$ ), 125.10 ( $\text{C}(1)$ ), 160.71 ( $\text{C}(2)$ ).  $^{29}\text{Si}$ - $\{^1\text{H}\}$  (500 MHz,  $\text{CDCl}_3$ ): –10.84. MS (EI):  $m/z$ , % = 367 (2) [ $\text{M}^+$ ], 293 (14), 263 (5), 219 (6), 138 (4), 73 (100), 45 (6).

**4.2.7. ((1E,3E)-2,3-Dioctylbuta-1,3-diene-1,4-diyl)bis(trimethylsilane) (2d).** Yield: 186 mg (84%);  $R_f$  = 0.7 (hexane). IR (liquid film): 2955, 2926, 2855, 1736, 1465, 1378, 1248, 840, 722, 690, 620  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 0.14 (s, 9H,  $\text{C}(11)\text{H}_3$ ), 0.91 (t,  $J$  = 7.2 Hz, 3H,  $\text{C}(10)\text{H}_3$ ), 1.29 (s, 12H,  $\text{C}(4-9)\text{H}_2$ ), 2.29 (t,  $J$  = 7.8 Hz, 2H,  $\text{C}(3)\text{H}_2$ ), 5.48 (s, 1H,  $\text{C}(1)\text{H}$ ).  $^{13}\text{C}$ - $\{^1\text{H}\}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 0.36 ( $\text{C}(11)$ ), 14.12 ( $\text{C}(10)$ ), 22.69 ( $\text{C}(9)$ ), 29.26 ( $\text{C}(4)$ ), 29.44 ( $\text{C}(5)$ ), 29.49 ( $\text{C}(7)$ ), 29.80 ( $\text{C}(6)$ ), 31.89 ( $\text{C}(8)$ ), 33.99 ( $\text{C}(3)$ ), 125.08 ( $\text{C}(1)$ ), 160.71 ( $\text{C}(2)$ ).  $^{29}\text{Si}$ - $\{^1\text{H}\}$  (500 MHz,  $\text{CDCl}_3$ ): –10.82. MS (EI):  $m/z$ , % = 423 (6) [ $\text{M}^+$ ], 422 (<1), 349 (15), 324 (9), 275 (6), 251 (7), 226 (5), 73 (100), 45 (3).  $\text{C}_{26}\text{H}_{54}\text{Si}_2$  calc. C 73.85, H 12.87; CHN analysis, C 74.3, H 12.5.

**4.2.8. ((1Z,3Z)-1,4-Diiodo-2,3-dioctylbuta-1,3-diene-1,4-diyl)bis(trimethylsilane) (4d).** Yield: 233 mg (69%);  $R_f$  = 0.7 (hexane).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 0.36 (s, 9H,  $\text{C}(11)\text{H}_3$ ), 0.91 (t,  $J$  = 6.9 Hz, 3H,  $\text{C}(10)\text{H}_3$ ), 1.29 (s, 8H,  $\text{C}(5,7-9)\text{H}_2$ ), 1.51–1.56 (m, 2H,  $\text{C}(6)\text{H}_2$ ), 1.51–1.56 (m, 1H(A),  $\text{C}(4)\text{H}_2$ ), 1.61–1.66 (m, 1H(B),  $\text{C}(4)\text{H}_2$ ), 2.22 (t,  $J$  = 0.0 Hz, 1H(A),  $\text{C}(3)\text{H}_2$ ), 2.47–2.54 (m, 1H(B),  $\text{C}(3)\text{H}_2$ ).  $^{13}\text{C}$ - $\{^1\text{H}\}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 1.88 ( $\text{C}(11)$ ), 14.12 ( $\text{C}(10)$ ), 22.68 ( $\text{C}(9)$ ), 28.83 ( $\text{C}(4)$ ), 29.26 ( $\text{C}(5)$ ), 29.28 ( $\text{C}(7)$ ), 30.18 ( $\text{C}(6)$ ), 31.84 ( $\text{C}(8)$ ), 36.54 ( $\text{C}(3)$ ), 100.56 ( $\text{C}(1)$ ), 163.72 ( $\text{C}(2)$ ). MS (EI):  $m/z$ , % = 675 (<1) [ $\text{M}^+$ ], 547 (7), 273 (11),

207 (100), 191 (11), 133 (9), 96 (16), 73 (88), 40 (13).  $\text{C}_{26}\text{H}_{52}\text{I}_2\text{Si}_2$  calc. C 46.29, H 7.77; CHN analysis, C 46.5, H 7.7.

**4.2.9. ((1E,3E)-2,3-Diphenylbuta-1,3-diene-1,4-diyl)bis(trimethylsilane) (2e).**<sup>21</sup> Yield: 106 mg (61%);  $R_f$  = 0.7 (hexane).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  = –0.28 (s, 9H,  $\text{C}(7)\text{H}_3$ ), 5.48 (s, 1H,  $\text{C}(1)\text{H}$ ), 7.22 (d,  $J$  = 6.9 Hz, 1H,  $\text{C}(4)\text{H}$ ), 7.31–7.38 (m, 2H,  $\text{C}(5,6)\text{H}$ ).  $^{13}\text{C}$ - $\{^1\text{H}\}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  = –0.28 ( $\text{C}(7)$ ), 126.88 ( $\text{C}(6)$ ), 127.57 ( $\text{C}(5)$ ), 129.91 ( $\text{C}(4)$ ), 133.90 ( $\text{C}(1)$ ), 142.16 ( $\text{C}(3)$ ), 159.87 ( $\text{C}(2)$ ). MS (EI):  $m/z$ , % = 351 (7) [ $\text{M}^+$ ], 350 (20), 335 (7), 276 (13), 262 (21), 247 (28), 135 (18), 73 (100), 45 (12).

**4.2.10. (1Z,2Z)-1,2-Bis(iodo(trimethylsilyl)methylene)cyclohexane (6).**<sup>22</sup> Yield: 199 mg (79%);  $R_f$  = 0.6 (hexane). IR (liquid film): 2953, 2930, 2896, 2854, 1567, 1460, 1442, 1421, 1406, 1250, 1075, 963, 936, 842, 758, 692, 627, 499  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 0.33 (s, 9H,  $\text{C}(5)\text{H}_3$ ), 1.52 (t,  $J$  = 9.2 Hz, 1H(A),  $\text{C}(4)\text{H}_3$ ), 1.92 (s, 1H(B),  $\text{C}(4)\text{H}_2$ ), 2.21 (t,  $J$  = 12.0 Hz, 1H(A),  $\text{C}(3)\text{H}_2$ ), 2.88 (d,  $J$  = 12.0 Hz, 1H(B),  $\text{C}(3)\text{H}_2$ ).  $^{13}\text{C}$ - $\{^1\text{H}\}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 1.74 ( $\text{C}(5)$ ), 29.13 ( $\text{C}(4)$ ), 36.42 ( $\text{C}(3)$ ), 101.65 ( $\text{C}(1)$ ), 165.99 ( $\text{C}(2)$ ).  $^{29}\text{Si}$ - $\{^1\text{H}\}$  (500 MHz,  $\text{CDCl}_3$ ): 0.95. MS (EI):  $m/z$ , % = 504 (<1) [ $\text{M}^+$ ], 377 (59), 289 (16), 161 (20), 97 (13), 73 (100), 45 (12).

**4.2.11. (1Z,2Z)-1,2-Bis(iodo(trimethylsilyl)methylene)cycloheptane (7).** Yield: 279 mg (82%);  $R_f$  = 0.6 (hexane). IR (liquid film): 2952, 2926, 2852, 1557, 1442, 1408, 1249, 1182, 1038, 899, 865, 839, 758, 693, 627, 480  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 0.34 (s, 9H,  $\text{C}(5)\text{H}_3$ ), 1.47–1.52 (m, 2H(A),  $\text{C}(4,6)\text{H}_3$ ), 1.56–1.63 (m, 2H(B),  $\text{C}(4,6)\text{H}_2$ ), 2.39–2.47 (m, 1H(A),  $\text{C}(3)\text{H}_2$ ), 2.62–2.68 (m, 1H(B),  $\text{C}(3)\text{H}_2$ ).  $^{13}\text{C}$ - $\{^1\text{H}\}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 1.64 ( $\text{C}(5)$ ), 26.91 ( $\text{C}(6)$ ), 28.31 ( $\text{C}(4)$ ), 34.26 ( $\text{C}(3)$ ), 104.51 ( $\text{C}(1)$ ), 165.88 ( $\text{C}(2)$ ). MS (EI):  $m/z$ , % = 518 (1).  $^{29}\text{Si}$ - $\{^1\text{H}\}$  (500 MHz,  $\text{CDCl}_3$ ): 0.96. [ $\text{M}^+$ ], 391 (54), 358 (4), 303 (8), 175 (17), 131 (17), 97 (20), 73 (100), 40 (55).  $\text{C}_{15}\text{H}_{28}\text{I}_2\text{Si}_2$  calc. C 34.76, H 5.44; CHN analysis, C 35.1, H 5.7.

## Conflicts of interest

The authors declare no competing financial interest.

## Acknowledgements

The study was supported by a grant from the Russian Science Foundation (project No. 19-73-20128). The synthesis of the starting substrates – 1-alkynylsilanes was carried out within the RF state assignment, reg. no. AAAA-A19-119022290009-3.

## References

- 1 V. H. Gessner, J. F. Tannaci, A. D. Miller and T. D. Tilley, Assembly of macrocycles by zirconocene-mediated, reversible carbon-carbon bond formation, *Acc. Chem. Res.*, 2011, **44**, 435–446.
- 2 E. Negishi, S. J. Holmes, J. M. Tour, J. A. Miller, F. E. Cederbaum, D. R. Swanson and T. Takahashi, *J. Am. Chem. Soc.*, 1989, **111**, 3336–3346.
- 3 E. Negishi, *Dalton Trans.*, 2005, 827–848.
- 4 E. Negishi, F. E. Cederbaum and T. Takahashi, *Tetrahedron Lett.*, 1986, **27**, 2829–2832.



- 5 S. Urrego-Riveros, I. Ramirez y Medina, D. Duvinage, E. Lork, F. D. Sönnichsen and A. Staubitz, *Chem.-Eur. J.*, 2019, **25**, 13318–13328.
- 6 J. Linshoeft, *Synlett*, 2014, **25**, 2671–2672.
- 7 U. Rosenthal and V. V. Burlakov, *Synthesis*, 2002, 355–389.
- 8 H. Sinn and G. Oppermann, *Angew. Chem., Int. Ed. Engl.*, 1966, **5**, 962–963.
- 9 H. Sinn and E. Kolk, *J. Organomet. Chem.*, 1966, **6**, 373–382.
- 10 W. Kaminsky and H. Sinn, *Justus Liebigs Ann. Chem.*, 1975, **1975**, 424–437.
- 11 W. Kaminsky and H.-J. Vollmer, *Justus Liebigs Ann. Chem.*, 1975, **1975**, 438–448.
- 12 W. Kaminsky, J. Kopf, H. Sinn and H.-J. Vollmer, *Angew. Chem., Int. Ed. Engl.*, 1976, **15**, 629–630.
- 13 E. Negishi, D. Y. Kondakov, D. Choueiry, K. Kasai and T. Takahashi, *J. Am. Chem. Soc.*, 1996, **118**, 9577–9588.
- 14 I. R. Ramazanov and R. N. Kadikova, *Kinet. Catal.*, 2020, **61**, 106–111.
- 15 I. R. Ramazanov, R. N. Kadikova, Z. R. Saitova and U. M. Dzhemilev, *Asian J. Org. Chem.*, 2015, **4**, 1301–1307.
- 16 T. V. Tyumkina, D. N. Islamov, L. V. Parfenova, S. G. Karchevsky, L. M. Khalilov and U. M. Dzhemilev, *Organometallics*, 2018, **37**, 2406–2418.
- 17 L. Brandsma and H. D. Verkuijsse, *Synthesis of acetylenes, allenes, cumulenes: a laboratory manual*, Elsevier SPC, Amsterdam-Oxford-New York, 1981.
- 18 M. J. Frisch, *et al.*, *Gaussian 09, Revision A.1*, Gaussian, Inc., Wallingford, CT, 2009.
- 19 U. M. Dzhemilev, A. G. Ibragimov, V. A. D'yakonov and R. A. Zinnurova, *Russ. J. Org. Chem.*, 2007, **43**, 176–180.
- 20 W. You, X. Yan, Q. Liao and C. Xi, *Org. Lett.*, 2010, **12**, 3930–3933.
- 21 Z. Xi, X. Liu, J. Lu, F. Bao, H. Fan, Z. Li and T. Takahashi, *J. Org. Chem.*, 2004, **69**, 8547–8549.
- 22 V. A. D'Yakonov, R. A. Tuktarova and U. M. Dzhemilev, *Russ. Chem. Bull.*, 2011, **60**, 1633–1639.

