

Straightforward synthesis of five-membered metallacycloallenes: 1-Zirconacyclopenta-2,3-diene compounds derived from 1,3-enynes*

Noriyuki Suzuki^{1,2,‡}, Taichiro Shimura¹, Yoshio Sakaguchi², and
Yoshiro Masuyama¹

¹Department of Materials and Life Sciences, Faculty of Science and Technology,
Sophia University, 7-1 Kioicho, Chiyoda-ku, Tokyo 102-8554, Japan; ²Advanced
Technology Support Division, RIKEN Advanced Science Institute, 2-1 Hirosawa,
Wako-shi, Saitama 351-0198, Japan

Abstract: A five-membered metallacycloallene complex, 1-zirconacyclopenta-2,3-diene, was prepared from low-valent zirconocene and 2,4-bis(trimethylsilyl)but-1-en-3-yne. The complex reacted with carbonyl compounds to afford alkynyl alcohols after hydrolysis via C=O insertion into Zr–C bond. Similarly, nitriles inserted into the Zr–C bond to give the corresponding ketones after hydrolysis. The insertion of C=O and CN selectively took place at zirconium-sp³ carbon of the metallacycle.

Keywords: cycloallenes; 1,3-enynes; 1-metallacyclopenta-2,3-dienes; metallacycles; zirconium.

INTRODUCTION

Stability of small cycloallene compounds

Allene compounds have three carbon atoms linearly aligned. Thus, the smaller the ring size of cycloallenes are, the more labile they are [1]. For example, hydrocarbyl cyclohexa-1,2-dienes, six-membered cycloallenes, have not been isolated to date. Cycloallenes can be more stable on replacement of one or more ring-members with heteroatoms such as silicon and phosphorus. A few six-membered heterocycloallenes have been isolated, and their molecular structures were unambiguously determined (Fig. 1) [2–4]. Hydrocarbyl cyclopenta-1,2-dienes, five-membered cycloallenes, were first reported by Balci and co-workers as short-lived species [5,6].

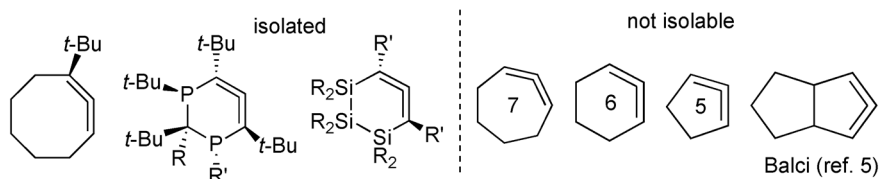


Fig. 1 Stability of cycloallenes.

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[‡]Corresponding author

Recently, we and Erker's group independently reported stable five-membered cycloallenes, 1-metallacyclopenta-2,3-diene compounds (Fig. 2) [7–12]. These complexes are stable at room temperature (rt). It should be noted that replacement of one carbon atom with a transition metal made the strained compounds much more stable, and it must be interesting to study their reactivity. The five-membered zirconacycloallene **1** was synthesized by transformation of a conjugated 1-zirconacyclopent-3-yne complex. The 1-zircona- and 1-hafnacyclopenta-2,3-dienes **2** were prepared from the corresponding bis(alkynyl)metallocenes via 1,1-hydroboration. The preparative methods of these complexes, however, were specific and unsuitable for large-scale synthesis. Therefore, more versatile synthetic routes have been desired in order to study the reactivity of five-membered metallacycloallenes. Bertrand and co-workers recently reported several bent allene compounds [13–15], including small cycloallenes. These compounds are of interest in relation to the metallacycloallenes, although the allene character of these is yet controversial [16,17].

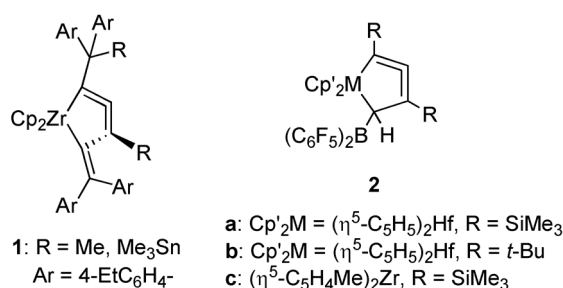
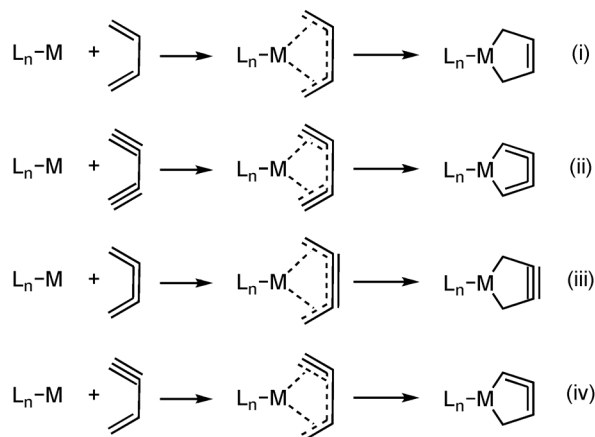


Fig. 2 1-Metallacyclopenta-2,3-dienes.

Straightforward synthesis of unsaturated metallacycles

For the syntheses of metallacyclic compounds such as 1-metallacyclopent-3-enes, 1-metallacyclopenta-2,3,4-trienes, and 1-metallacyclopent-3-yne, low-valent metallocenes and 1,3-dienes, 1,3-diynes, and 1,2,3-trienes are employed (i–iii, Scheme 1) [8]. This methodology realized the synthesis of stable five-membered metallacyclopentatrienes (ii) [18–20], as well as metallacycloalkynes (iii) [21–24], which have been thought to be highly reactive and unisolable. According to these protocols one must consider that 1,3-enynes would be possible starting compound for cycloallenes (iv, Scheme 1), as predicted by



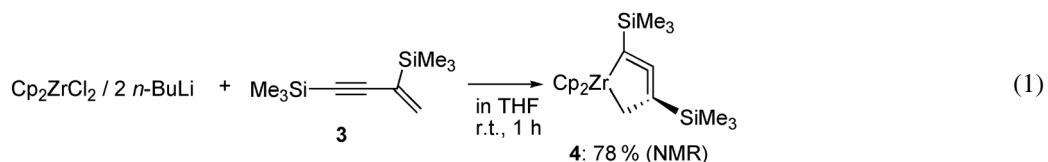
Scheme 1 Formation of unsaturated five-membered metallacycles.

Rosenthal for the reaction of zirconocene with 1,3-enynes [12]. But only a few reports on η^4 -enyne complexes have been known [25,26], and the possibility of 1-metallacyclopenta-2,3-diene has not been mentioned in these reports. It was reported, for example, that decamethyltitanocene, $(C_5Me_5)_2Ti$, forms with 2,4-bis(trimethylsilyl)but-1-en-3-yne only a η^2 -alkyne complex [27].

We examined, in fact, reactions of low-valent zirconocenes with a variety of 1,3-enynes, but most of these attempts were disappointing and resulted in a mixture of several products. A major problem in these reactions seems to be dimerization of 1,3-enynes at the metal center. We reasoned that bulky substituents at 2,4-positions of 1,3-enynes might suppress the undesired dimerization. Herein we report the synthesis of 1-metallacyclopenta-2,3-diene from a 1,3-enyne and the reactivity of the metallacycloallene compounds.

RESULTS AND DISCUSSION

We employed 2,4-bis(trimethylsilyl)but-1-en-3-yne (**3**) [28] as the 1,3-enyne of bulky substituents. The 1,3-enyne **3** was treated with Negishi reagent $[Cp_2Zr(n-Bu)_2]$ in tetrahydrofuran (THF). After stirring at rt for 1 h, the formation of 1-zirconacyclopenta-2,3-diene **4** was observed by 1H NMR (78 %, eq. 1). Complex **4** was fully characterized by 1H and ^{13}C NMR spectroscopy. Two singlets assignable to the Cp rings were observed at 5.13 and 5.35 ppm, and geminal nonequivalent protons at Zr- CH_2 appeared at 1.35 and 2.92 ppm, being coupled with each other by 8 Hz, indicating its molecular chirality. ^{13}C NMR spectroscopy showed that two quaternary carbons at 79.5 and 119.2 ppm were coupled with silicon atoms by 65 and 73 Hz, respectively. A "central" carbon of allene was observed at 135.1 ppm, which is in the same range as those of the previous examples (128.8 ppm for **1** (R = Me), 136.2 ppm for **2a**). Complex **4** is considerably stable in solution, and remained unchanged for a few days at rt. Our attempts to isolate **4** as crystals, however, have been unsuccessful. A solution of Cp_2ZrCl_2 and **3** may be sonicated in the presence of magnesium powder, although it resulted in modest yields. These results demonstrated that this is the promising method for the straightforward preparation of 1-metallacyclopenta-2,3-dienes from 1,3-enynes. We have attempted to employ a few other 1,3-enynes, however, satisfactory results have not been obtained so far because of instability of these 1,3-enynes [29].



Erker and co-workers indicated that complex **2a** (M = Hf) showed fast epimerization at 90 °C [9], and so did **2c** (M = Zr) at ambient temperature [10]. NMR observation of **4** demonstrated, on the other hand, that two Cp signals did not coalesce at 100 °C, indicating very slow epimerization of **4** (Fig. 3), as observed for **1**. These results implied that a borane substituent at α -position was responsible for fast epimerization in Erker's cycloallene compounds.

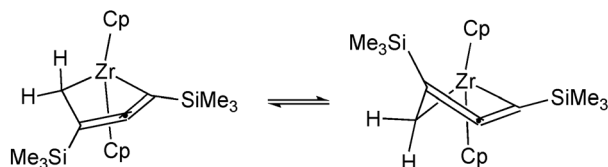
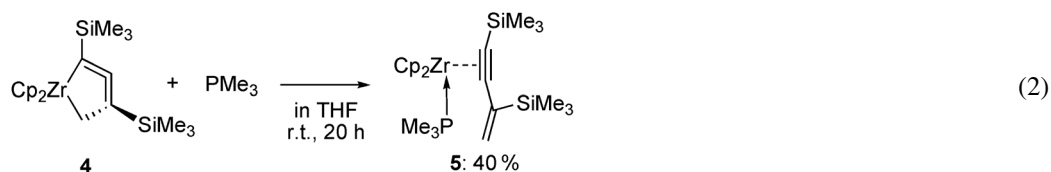
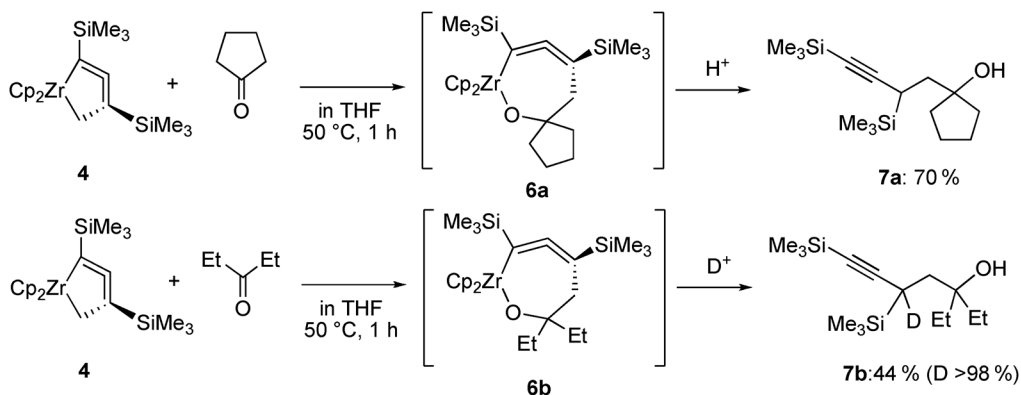


Fig. 3 Possible epimerization of **4** (not observed at 100 °C).

It is noteworthy that addition of trimethylphosphine to **4** resulted in disappearance of **4** in 20 h at rt. Instead, in ^1H NMR observation, one doublet assignable to Cp ligands appeared at 5.25 ppm with $^3J_{\text{P-H}} = 1.7$ Hz. This result suggests the formation of the phosphine-coordinated complex **5** in which the enyne **3** coordinated to the metal in an η^2 -fashion (eq. 2). Indeed, two doublets assignable to the geminal vinyl protons were observed at 4.73 and 4.75 ppm with $J = 3.8$ Hz. The yield of **5** was estimated by ^1H NMR (40%). It should be noted that the transformation from **4** to **5** can be regarded as a haptotropic shift of 1,3-enyne on the metal. It is in a sharp contrast to metallacycloalkyne complexes, 1-zirconacyclopent-3-yne, in which haptotropic shift of cumulene ligands are rarely observed [30].



The reactivity of the metallacycloallene **4** toward carbonyl compounds was examined. Complex **4** reacted with cyclopentanone at rt to afford an alkynyl alcohol **7** after hydrolysis (Scheme 2). Presumably, the C=O double bond inserted into the Zr–C bond to form the seven-membered oxazirconacycloallene intermediate **6**. A reaction with 3-pentanone also took place. Deuterolysis with $\text{DCI}/\text{D}_2\text{O}$ afforded the alcohol **7b** that has deuterium (>98%) at α -position to the silyl group. On the other hand, aldehydes, such as benzaldehyde, did not give satisfactory results although the reason is unclear yet.



Scheme 2 Reaction of **4** with ketones.

One might suggest another possible intermediate **6'** for this reaction (Fig. 4). The alcohol **7** can be obtained by the reaction at γ -position in seven-membered oxazirconacycloheptadiene **6**, while attack on the α -position in five-membered α -alkynylloxazirconacyclopentane **6'** can give **7**. It has been known that propargyl and allenyl zirconium species favor γ -position over α -position in the reactions with electrophiles [31]. In addition, it is unlikely that species **6'** is stable enough for steric demand at the substituted α -position. NMR observation of the reaction solution showed ^{13}C signal at 173 ppm, which might be assignable to the central carbon of allene moiety of **6**.

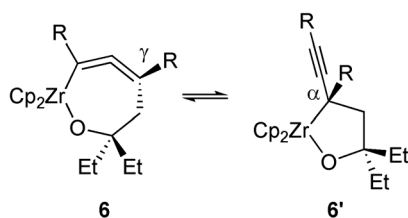
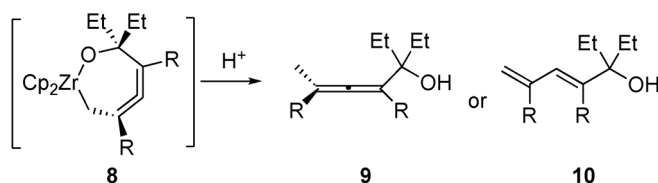


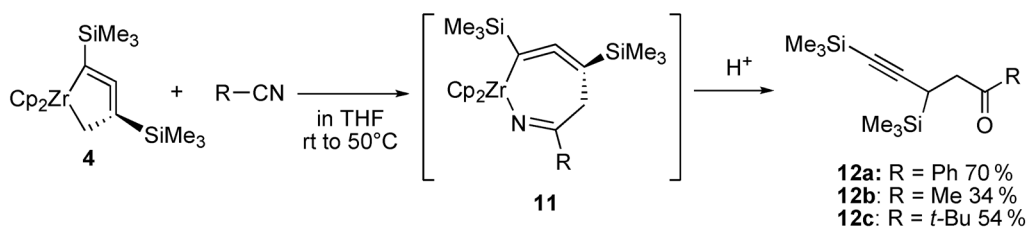
Fig. 4 Possible intermediates for C=O inserted species.

It is noteworthy that the insertion occurred selectively at zirconium- sp^3 carbon. Insertion of carbonyl compounds at zirconium- sp^2 carbon must give the intermediate **8** (Scheme 3), which will give alcohol **9** or **10** after hydrolysis. But these possible isomers were not observed by gas chromatography. This result is consistent with the reactions of 1-zirconacyclopent-2-enes and aldehydes shown by Negishi, Takahashi, and co-workers, in which carbonyl C=O selectively inserted into zirconium- sp^3 carbon [32].



Scheme 3 Possible intermediate via the reaction at zirconium- sp^2 carbon.

Reaction of **4** with nitriles also took place at zirconium- sp^3 carbons, and alkynyl ketones were obtained after hydrolysis (Scheme 4). Intermediate **11** was observed by NMR spectroscopy, showing that it was a seven-membered azazirconacycloallene. In ^1H NMR spectra, unequivalent Cp signals were observed at 5.84 and 5.86 ppm and two singlets for trimethylsilyl groups at 0.04 and 0.23 ppm. Geminal protons of CH_2 appeared at 2.20 and 3.92 ppm with $J = 14.4$ Hz. Two quaternary carbons were observed at 169.7 and 171.7 ppm, one of these must be assignable to the central carbon of allene and the other to the imine. This observation is in sharp contrast to the results reported by Erker and co-workers. They reported insertion of nitrile into the zirconium- sp^3 carbon bond in the 1-zirconacyclopenta-2,3-diene [11]. In their results, a zwitter ionic alkyne-coordinated complex formed instead of a seven-membered azametallacycloallene. It is probably due to the presence of borane groups at the ring structure. It is noteworthy that Xi and co-workers recently reported the zirconium complex of a structure similar to **11** by a different preparative method [33].



Scheme 4 Insertion of nitriles into Zr-C bond in metallacycloallene.

In conclusion, we found straightforward synthetic method of 1-zirconacyclopenta-2,3-diene compound, five-membered metallacycloallene, from low-valent zirconocene and 2,4-bis(trimethylsilyl)but-1-en-3-yne. Ketone inserted into zirconium-sp³ carbon bond selectively to afford alkynyl alcohol after hydrolysis. So did nitrile to give the corresponding ketone after hydrolysis. Seven-membered oxa- and azazirconacycloallene intermediates are suggested.

EXPERIMENTAL

General

All manipulations on organometallic compounds were carried out under an inert atmosphere using Schlenk technique or in a glove box. Anhydrous THF and hexane were purchased from Kanto Chemical Co., Inc. and degassed prior to use. Dichlorobis(η^5 -cyclopentadienyl)zirconium was purchased from Sigma-Aldrich. NMR spectra were recorded on JEOL Lambda 300 and Lambda 500 spectrometer. 2,4-Bis(trimethylsilyl)but-1-en-3-yne (**3**) was prepared according to the literature method [28].

Synthesis of 1,1-bis(η^5 -cyclopentadienyl)-2,4-bis(trimethylsilyl)-1-zirconacyclopenta-2,3-diene (**4**)

To a solution of dichlorobis(η^5 -cyclopentadienyl)zirconium (292 mg, 1.0 mmol) in THF (5 mL) was added *n*-butyllithium (1.6 M hexane solution, 2 mmol) at -78 °C. After the reaction mixture was stirred for 1 h, **3** (196 mg, 1.0 mmol) was added. After removal of dry ice bath, the mixture was allowed to warm up to rt and was stirred for additional 1 h. ¹H NMR spectroscopy indicated the formation of the title compound in 78 % yield in this stage. For reaction with ketones and nitrile, this reaction mixture was used. ¹H NMR (300 MHz, C₆D₆): δ 0.19 (s, 9H, SiCH₃), 0.31 (s, 9H, SiCH₃), 1.35 (d, *J* = 8 Hz, 1H, CH₂), 2.92 (d, *J* = 8 Hz, 1H, CH₂), 5.13 (s, 5H, Cp), 5.35 (s, 5H, Cp). ¹³C NMR (75 MHz, C₆D₆, Me₄Si): δ -0.44 (CH₃), 1.58 (CH₃), 47.55 (CH₂), 79.45 (q, *J*_{Si-C} = 65 Hz), 100.70 (Cp), 104.83 (Cp), 119.20 (q, *J*_{Si-C} = 73 Hz, Zr-C), 135.11 (q, C=C=C).

Synthesis of bis(η^5 -cyclopentadienyl)zirconium[τ^2 -2,4-bis(trimethylsilyl)but-1-en-3-yne](trimethylphosphine) (**5**)

A solution of **4** in THF (5 mL) was prepared as described above using 1.0 mmol of dichlorobis(η^5 -cyclopentadienyl)zirconium. To this solution was added trimethylphosphine (148 mg, 1.94 mmol) at rt, and the mixture was stirred for 20 h. The formation of **5** was observed by ¹H NMR spectroscopy (40 %). ¹H NMR (300 MHz, THF/C₆D₆): δ 0.00 (s, 9H), 0.13 (s, 9H), 1.25 (d, 9H, ²*J*_{P-H} = 6.2 Hz, PCH₃), 4.73 (d, *J* = 3.8 Hz, 1H), 4.75 (d, *J* = 3.8 Hz, 1H), 5.25 (d, ³*J*_{P-H} = 1.7 Hz, 10H, Cp).

Reaction 4 with ketones: Preparation of alkynyl alcohols

Typical procedure is as follows. To a solution of **4** (0.7 mmol) in THF (5 mL) was added cyclopentanone (65 mg, 0.77 mmol) at rt. The mixture was stirred at 50 °C for 1 h, then treated with 1N HCl and extracted with diethyl ether. Organic layer was dried with MgSO₄ and volatiles were removed in vacuo. The residue was then purified by column chromatography using silica gel (hexane/ethyl acetate = 9/1). The alkynyl alcohol, 1-[2,4-bis(trimethylsilyl)but-3-ynyl]cyclopentanol (**7a**), was obtained as colorless oil (70 %). **7a**: ¹H NMR (300 MHz, C₆D₆, Me₄Si): δ 0.08 (s, 9H), 0.17 (s, 9H), 1.21–1.26 (m, 2H), 1.50–1.58 (m, 6H), 1.89–1.96 (m, 3H, CH, CH₂). ¹³C NMR (75 MHz, C₆D₆, Me₄Si): δ -3.49, 0.26, 17.67 (CH), 23.93, 24.40, 31.94, 39.70, 40.67 (CH₂ × 5), 83.75 (q, COH), 86.61 (q, C≡CSi), 111.19 (q, C≡CSi). IR (NaCl): 636, 694, 841, 1076, 1250, 1732, 1906, 2152, 2958 (cm⁻¹). HRMS calcd. for C₁₅H₃₀OSi₂ = 282.1835, found 282.1831.

3-Ethyl-5,7-bis(trimethylsilyl)hept-6-yn-3-ol (7b)

Colorless oil (44 %). ^1H NMR (300 MHz, C_6D_6 , Me_4Si): δ 0.08 (s, 9H), 0.16 (s, 9H), 0.82 (t, $J = 7.6$ Hz, 3H), 0.94 (t, $J = 7.6$ Hz, 3H), 1.43 (dd, $J = 14$, 2 Hz, 1H, CH_2), 1.46–1.62 (m, 4H, CH_2), 1.71 (dd, $J = 14$, 12 Hz, 1H, CH_2), 1.83 (dd, $J = 12$, 2 Hz, 3H, CH_2). ^{13}C NMR (75 MHz, C_6D_6): δ -3.51, 0.26, 8.17, 8.42, 15.90 (CH), 30.98 (CH_2CH_3), 31.45, 36.83 ($\text{CH}_2 \times 3$), 75.60 (q, COH), 86.04 (q, $J_{\text{Si-C}} = 86$ Hz, $\text{C}\equiv\text{CSi}$), 110.93 (q, $\text{C}\equiv\text{CSi}$). IR (NaCl): 636, 698, 840, 1250, 1458, 1732, 1906, 2152, 2962 (cm^{-1}). HRMS calcd. for $\text{C}_{15}\text{H}_{32}\text{OSi}_2 = 284.1992$, found 284.1993.

Reaction 4 with nitriles: Preparation of alkynyl ketones

Typical procedure is as follows. To a solution of **4** (0.7 mmol) in THF (5 mL) was added benzonitrile (146 mg, 1.4 mmol) at rt. The mixture was stirred for 1.5 h, then treated with 1N HCl and extracted with diethyl ether. Organic layer was dried with MgSO_4 and volatiles were removed in vacuo. The residue was then purified by column chromatography using silica gel (hexane/ethyl acetate = 9/1). The alkynyl ketone, 1-phenyl-3,5-bis(trimethylsilyl)pent-4-yn-1-one (**12a**), was obtained as reddish solid (70 %). **12a**: ^1H NMR (300 MHz, CDCl_3 , Me_4Si): δ 0.071 (s, 9H), 0.14 (s, 9H), 2.46 (dd, $J = 9$, 5 Hz, 1H, CH), 2.94 (dd, $J = 16.5$, 5 Hz, 1H, CH_2), 3.23 (dd, $J = 16.5$, 9 Hz, 1H, CH_2), 7.44–7.65 (m, 3H), 7.95–7.98 (m, 2H). ^{13}C NMR (75 MHz, CDCl_3 , Me_4Si): δ -3.08, 0.37, 16.74 (CH), 38.66 (CH_2), 85.08 (q), 108.6 (q), 128.39, 128.66, 133.13, 137.21 (q), 198.82 (q). IR (KBr): 691, 895, 1092, 1250, 1682, 2145, 2959 (cm^{-1}). HRMS calcd. for $\text{C}_{17}\text{H}_{26}\text{OSi}_2 = 302.1522$, found 302.1522.

4,6-Bis(trimethylsilyl)hex-5-yn-2-one (12b)

The reactions were similarly carried out using acetonitrile at rt for 3 h, and for additional 1 h at 50 °C; yellow oil (34 %). ^1H NMR (300 MHz, CDCl_3 , Me_4Si): δ 0.09 (s, 9H), 0.11 (s, 9H), 2.19 (dd, $J = 10$, 4 Hz, 1H, CH), 2.22 (s, 3H), 2.39 (dd, $J = 16$, 4 Hz, 1H, CH_2), 2.57 (dd, $J = 16$, 10 Hz, 1H, CH_2). ^{13}C NMR (75 MHz, CDCl_3 , Me_4Si): δ -3.46, 0.22, 16.74 (CH), 30.17 (CH_3), 43.26 (CH_2), 85.12 (q), 108.21 (q), 207.67 (q). IR (NaCl): 636, 698, 806, 1022, 1250, 1358, 1412, 1720, 1913, 21660, 2901, 2959 (cm^{-1}). HRMS calcd. for $\text{C}_{12}\text{H}_{24}\text{OSi}_2 = 240.1366$, found 240.1365.

2,2-Dimethyl-5,7-bis(trimethylsilyl)hept-6-yn-3-one (12c)

The title compounds were similarly prepared to described above using pivalonitrile at rt for 3 h; colorless oil (54 %). ^1H NMR (300 MHz, CDCl_3 , Me_4Si): δ 0.086 (s, 18H), 0.15 (s, 9H), 2.31–2.38 (m, 2H), 2.81 (dd, $J = 10$, 8 Hz, 1H). ^{13}C NMR (75 MHz, CDCl_3 , Me_4Si): δ -3.17, 0.32, 16.02 (CH), 26.31 (CCH_3), 36.67 (CH_2), 44.01 (q), 84.19 (q), 109.24 (q), 213.79 (q). IR (NaCl): 640, 760, 972, 1007, 1065, 1250, 1477, 1713, 2160, 2959 (cm^{-1}). HRMS calcd. for $\text{C}_{15}\text{H}_{30}\text{OSi}_2 = 282.1835$, found 282.1837.

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