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TITANIUM-CATALYZED DIELS–ALDER CYCLOADDITION OF CONJUGATED DIENES TO BIS(TRIMETHYLSILYL)ACETYLENE. 1,2-BIS(TRIMETHYLSILYL)CYCLOHEXA-1,4-DIENE, 1,2-BIS(TRIMETHYLSILYL)BENZENE, AND THEIR METHYL DERIVATIVES

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Summary

The catalytic system $Et_2AlCl/TiCl_4$ induces Diels–Alder cycloaddition of bis(trimethylsilyl)acetylene to 1,3-butadiene, isoprene, 2,3-dimethyl-1,3-butadiene and (*E*)-1,3-pentadiene affording 1,2-bis(trimethylsilyl)cyclohexa-1,4-dienes in high yields. The cyclohexadienes are readily converted to the corresponding 1,2-bis(trimethylsilyl)benzenes upon heating to 240°C. Mass, infrared, ^{1}H, ^{13}C and ^{29}Si NMR spectra of all the products obtained are reported and briefly discussed. The crowded character of aromatic compounds is reflected in their mass, ^{13}C and ^{29}Si NMR spectra.

Introduction

The Diels–Alder reaction between non-polar dienes and acetylenes usually requires high temperature activation which in turn decreases the regio- and stereoselectivity of the process. Highly selective cycloadditions have been carried out under mild conditions by transition metal catalysts. Nickel-catalyzed reactions have been reported to yield diene-acetylene cyclic adducts in 2/1, 2/2 and 1/2 ratios, depending on the ligand field of nickel complex [1]. The 1/1 cyclic adducts have

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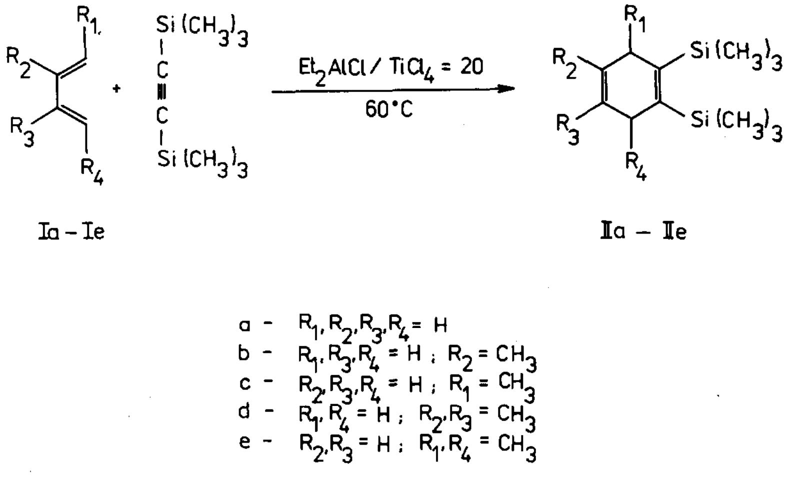
been obtained with iron-based catalysts, e.g., dicyclooctatetraeneiron [2] and the (1,4-diaza-1,3-diene)iron dichloride/triethylaluminium systems [3].

The titanium catalysts are known to catalyze linear dimerization [4], cyclotrimerization [5–7] and polymerization of various acetylenes [8–10]. Besides, we have recently discovered that under catalysis by the $Et_2AlCl/TiCl_4$ system some disubstituted acetylenes enter the [6 + 2] cycloaddition reaction with 1,3,5-cycloheptatriene, competing with their cyclotrimerization [11,12]. Among acetylenes, only bis(trimethylsilyl)acetylene (BTMSA) did not show a tendency to catalytic homo-oligomerization and reproducibly gave a high yield of the [6 + 2] adduct, 7,8-bis(trimethylsilyl)bicyclo[4.2.1]nona-2,4,7-triene. This unique property indicated that BTMSA might be an ideal dienophile for a variety of cycloaddition reactions.

In this paper we report the Diels–Alder reaction of BTMSA with conjugated dienes catalyzed by the $Et_2AlCl/TiCl_4$ system and give spectroscopic characterization of the resulting derivatives of 1,2-bis(trimethylsilyl)cyclohexa-1,4-diene and aromatic compounds derived from them.

Results and discussion

The [4 + 2] cycloaddition of BTMSA with conjugated dienes Ia–Ie proceeded under catalysis by the $Et_2AlCl/TiCl_4$ system (Al/Ti = 20) in aromatic solvents according to Scheme 1. Using optimized molar ratios BTMSA/Ti = 120 and BTMSA/diene = 1.1, high yields of cyclohexadienes IIa–IId were obtained; only (*E*,*E*)-2,4-hexadiene afforded IIe in a low yield (see Table 1). If a molar excess of dienes was used the content of low-molecular by-products considerably increased in the cases of IIa, IIb and IId, while the purity of IIc and IIe was influenced negligibly (Table 1), since the by-products of IIc and IIe were polymers. The yields of cyclohexadienes depended mainly on the order of component mixing. The optimum yields, given in Table 1, were obtained when BTMSA was dosed in 5 min after mixing solutions of $TiCl_4$ and Et_2AlCl and then the diene was added after another 5 min. Among compounds II only IIb was previously prepared in a low yield [3],



SCHEME 1

TABLE 1

DEPENDENCE OF YIELD AND PURITY OF THE DIELS–ALDER PRODUCT ON THE MOLAR RATIO BTMSA/DIENE [a]

Diene	BTMSA/ diene	Crude product II		By-products in crude II	Non-volatile by-products [c]
		Yield (%) [b]	Purity (%)		
Ia	1.04	78	94	(*Z*,*E*,*E*)-1,5,9-Cyclododecatriene (CDT) and (*E*,*E*,*E*)-CDT (1/1)	(*Z*)-1,4-Poly(butadiene)
	0.52	62	76		
Ib	1.2	72	92	1,4-Dimethyl-4-vinylcyclohex-1-ene ≈ Dimethylcycloocta-1,5-diene	Trimethyl-1,5,9-CDT and polymer
	0.6	60	70		
Ic	1.2	76	99		(*E*)-1,4-Poly(1,3-pentadiene) [d]
	0.6	61	97		
Id	1.35	72	96	2,3,6,7-Tetramethylocta-1,3,6-triene	Trimer and polymer
	0.67	55	53		
Ie	1.35	15	98		(*E*)-2,5-Poly(2,4-hexadiene) [c]
	0.67	15	96		

[a] Experimental conditions: $TiCl_4$ 0.1 mmol, Et_2AlCl 2.0 mmol, benzene 5 ml, BTMSA 12 mmol, diene 8.8–11.5 mmol and 17.6–23.0 mmol, 60°C, 6 h. [b] The diene conversion was always 100% in experiments using a BTMSA/diene ratio ca. 1 according to GLC analysis; the yields of II are lowered by losses during benzene and BTMSA evaporation in vacuo. [c] The distribution of diene homooligomers and polymers was not affected observably by the presence of BTMSA; no trimethylsilyl groups were found in the diene polymers. [d] According to IR spectrum (film): 3013w, 1449, 1368, 966vs cm^{-1}. [e] According to IR spectrum (film): 3020w, 1449, 1368, 966vs cm^{-1}.

however, its mass spectrum was characteristic for 1,2-bis(trimethylsilyl)-4-methylbenzene, the product of dehydrogenation of IIb (cf. mass spectra given below).

The catalytic system

Mixing of the catalyst components in benzene afforded a heterogeneous system containing a rusty brown precipitate. The addition of BTMSA resulted in slow dissolution of the precipitate and formation of a clear green solution. This process was speeded up by warming to 60°C for 15 min. The green complex, exhibiting a strong absorption band at 620 nm, can be suggested to be catalytically active in the cycloaddition reaction, for when the dienes had been added to its solution the products II were formed in yields close to those given in Table 1. During the cycloaddition reaction the green complex decomposed, which was indicated by diminution of the absorption band at 620 nm.

ESR measurement of the system after addition of BTMSA at −78°C, while warming to room temperature showed primary formation of a broad ESR signal ΔH 2.0 mT at $g = 1.955$ followed by appearence of another signal at $g = 1.973$ (ΔH 1.3 mT). No vinyl radical [13] or acetylene radical ion [14] ESR signals were detected near $g = 2.003$. The intensity of the signal at $g = 1.955$ decreased slowly at room temperature and the signal disappeared upon warming the sample to 60°C. The latter signal may be tentatively assigned to a transient monomeric titanium(III) chloride which became soluble due to simultaneous solvation by BTMSA and Et_2AlCl. The intensity of the signal at $g = 1.973$ increased slightly after warming the sample to 60°C, but this change was clearly related neither to the disappearance of the former ESR signal nor to the occurrence of the absorption band at 620 nm. This signal could belong to a stable product of the catalyst side reaction, since it persisted after completing the BTMSA-diene addition when the absorption band at 620 nm had already disappeared. A quantitative estimate of concentrations of both ESR-active species revealed that they accounted for less than 10% of the overall titanium concentration which, along with the above evidence, confirmed that the green, soluble titanium complex was diamagnetic.

We suggest that the green complex is a titanium(II) compound structurally analogous to the species which has been proposed to catalyze the [6 + 2] cycloaddition reactions of cycloheptatriene [12]. Instead of a η-coordinated 1,3,5-cycloheptatriene it probably contains two η-coordinated BTMSA molecules, and the [4 + 2] cycloaddition reaction occurs when one BTMSA molecule is replaced by the diene molecule. The coordination of BTMSA is in all cases stronger than that of dienes, as the green complex is not replaced by complexes typical for interaction of the diene itself with this catalytic system, e.g., the red-coloured complexes of 1,3-pentadiene and 2,4-hexadiene.

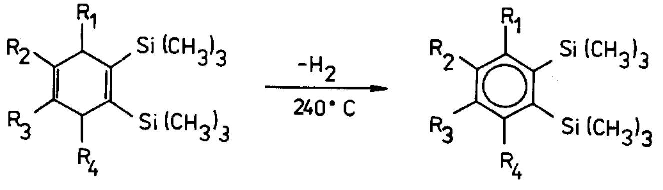
So far we did not succeeded in isolation of the greenish-brown, nonparamagnetic product of the catalyst deactivation which shows only decreasing continuous absorption from 400 to 1000 nm. However, in contrast to the cyclotrimerization of diphenylacetylene with catalytic systems based on C_8H_8TiCl or $TiCl_3$, where tetraphenyltitanacyclopentadiene compounds were determined to be the products of deactivation [15,16], the resistance of bulky BTMSA to homooligomerize makes the formation of analogous tetrakis(trimethylsilyl)titanacyclopentadiene compounds improbable.

Aromatization of 1,2-bis(trimethylsilyl)cyclohexa-1,4-dienes

In comparison with cyclohexa-1,4-diene the adducts II showed higher stability against polymerization, while they underwent thermal dehydrogenation under evolution of molecular hydrogen. Heating of II to 240°C in large evacuated ampoules afforded 1,2-bis(trimethylsilyl)benzene (IIIa) and its methyl derivatives IIIb–IIId (Scheme 2) in nearly theoretical yields. The conversion of II to III proceeded quantitatively without positional isomerization of substituents only if compounds II were pure and dry; otherwise the presence of positional isomers was detected by the GC/MS method. In this series only IIIa was previously prepared by the Diels–Alder reaction of α-pyrone with BTMSA [17].

Spectroscopical characteristics of products

The products II and III were characterized by infrared (IR), mass (MS) and ^1H, ^{13}C and ^{29}Si NMR spectra. The MS and ^{29}Si NMR spectra are discussed in more



IIa - IId   IIIa - IIId

SCHEME 2

detail because they reflect the crowded character of compounds which is especially remarkable in the aromatic compounds III.

The infrared spectra of all compounds show very strong bands of the $(CH_3)_3Si$ group below 3000 cm^{-1}, at 1260–1240 cm^{-1} and in the region of 840–744 cm^{-1}. The valence vibrations ν(=C–H) in the 3000–3100 cm^{-1} region were observed for IIa–IIc and IIe and for all the aromatic compounds. The overtone bands of the substituted aromatic ring at 1600–2000 cm^{-1} were of very low intensity and their detailed study would have required high purity compounds. The IR spectra (see Experimental) are represented by the "finger print" bands of medium-to-low intensity occurring in the 1200–400 cm^{-1} region which are valuable for identification of individual compounds.

The mass spectra show the following main features. In the case of cyclohexadienes IIa–IIe trimethylsilylium ions dominate the spectra; $[M-CH_3]^+$ and $[M-Si(CH_3)_3]^+$ ions are of moderate or low abundances while the ions $[M-H]^+$ are of very low abundance. The retro-Diels–Alder decomposition is observed with all the cyclohexadienes except IIa; the positive charge is localized on the diolefinic part. However, all the compounds exhibited $C_7H_{15}Si_2{}^+$ ions arising very probably as common yne-fragments by a retro-Diels–Alder fragmentation of $[M-CH_3]^+$. 1,2-Bis(trimethylsilyl)benzene derivatives IIIa–IIId form $[M-CH_3-CH_4]^+$ as the base peak, and abundant $[M-CH_3]^+$ ions; the formation of both may be related to the presence of bulky trimethylsilyl groups in the *ortho* position. It is also noteworthy that doubly charged $[M-2CH_3-CH_4]^{2+}$ ions are produced in greater relative abundance than $[M-2CH_3]^{2+}$. As expected, $(CH_3)_3Si^+$ ions are prominent fragments, accompanied by ions formed from $[M-CH_3]^+$ by elimination of $CH_2{=}Si(CH_3)_2$.

In the NMR spectra of aromatic compounds, it has been established [18] that the *ortho* trimethylsilyl group brings about a strong deshielding effect on the ^{29}Si chemical shift, whilst the *ortho* methyl group exerts an opposite shielding effect. The *ortho* substituents are also responsible for large and opposite deviations of chemical shifts predicted according to the additivity rule [18]. These conclusions appear to be fully valid for ^{29}Si and ^{13}C NMR spectra of the aromatic compounds III. The large deshielding effect of the *ortho* trimethylsilyl group was only slightly influenced by the shielding effect of methyl groups in *meta* and *para* positions, while the *ortho* methyl group in IIIc induced the difference in chemical shifts of the two silicon nuclei as large as 2.8 ppm. In accordance with ref. 18, the high-field signal of the ^{29}Si NMR spectrum of IIIc can be assigned to the silicon atom vicinal to the methyl group. The deviation from additivity of aromatic carbon chemical shifts and the small changes in shielding of carbon atoms of the trimethylsilyl groups allow to suggest that the large *ortho* effect may be due to a release of steric strain by aromatic ring deformation.

Analogous discussion of similar trends in the spectra of 1,4-cyclohexadiene derivatives II is not yet possible, because the data for comparable model compounds are not available and the observed effects are small. The smaller effects of the substituents in these compounds compared to the aromatic compounds are in agreement with both better transmission of electronic effects through the benzene ring and lower steric hindrance in the 1,4-cyclohexadiene skeleton and its higher conformational mobility.

Experimental

Chemicals

$TiCl_4$ (Intern. Enzymes Ltd.) was distilled in vacuo and diluted with benzene to give a 0.1 *M* solution. Et_2AlCl (Fluka) was purified by distillation in vacuo and used as a 1.0 *M* solution in benzene. Benzene was purified in the same manner as that used for the catalytic cyclotrimerization of butadiene [19]. Bis(trimethylsilyl)acetylene (Fluka) was distilled twice in vacuo. Dienes were purified with the corresponding η^3-allyltitanocene compounds as described elsewhere [20].

Methods

The gas chromatographic analyses were carried out on a Perkin–Elmer F-21 preparative gas chromatograph using Carbowax M-20 (10% on Chromaton N-AW) and SE-30 (15% on Chromaton N-AW) columns (4 m, 10 mm). The mass spectra were recorded on a JEOL JMS D-100 spectrometer at 75 eV, using gas chromatograph/mass spectrometer coupling or capillary dosing from a direct inlet. The ESR spectra were taken on an ERS-220 spectrometer (German Academy of Sciences, Berlin, GDR) in the X-band using a variable temperature unit. Infrared spectra of thin film samples were recorded on a UR-75 spectrometer (Zeiss, Jena). The electronic absorption spectra were taken on a Varian Cary 17 D spectrometer using sealed quartz cuvettes. ^1H and ^{13}C NMR spectra were measured on a JEOL FX-60 spectrometer at 59.797 and 15.036 MHz, respectively, and on a Varian XL-200 spectrometer (50.309 MHz for ^{13}C). Multiplicities given in ^{13}C NMR spectra were determined from single frequency off-resonance (SFORD), noise off-resonance (NORD) or proton-coupled spectra. ^{29}Si NMR spectra were taken on a Varian XL-200 spectrometer using a routine version of the INEPT pulse sequence [21]. FIDs were registered with spectral width of 4.0 kHz utilizing a 16 k memory system. Small exponential weighting corresponding to line broadening of 1.0 Hz was used prior to Fourier transformation. The spectra were referenced to the line of hexamethyldisilane (δ -9.79 ppm) which was added to the measured $CDCl_3$ solutions (3% v/v). The chemical shift values in δ scale are estimated to be precise within ± 0.02 ppm.

Catalyzed Diels–Alder cycloadditions

Benzene solutions of $TiCl_4$ (0.1 *M*, 1 ml), Et_2AlCl (1.0 *M*, 2 ml), BTMSA (3.0 *M*, 4 ml) and the diene (1 ml, 8.8–11.5 mmol) were placed in this order into the reaction ampoule by opening breakable seals in an all-glass evacuated device. After opening the diene containing ampoule the reaction mixture was cooled by liquid nitrogen and sealed off. The ampoule was warmed while shaking and kept in a water bath at 60°C for 6 h. After opening to air the reaction mixture was diluted with benzene (20 ml) and washed with water. The organic layer was separated, dried with Na_2SO_4 and distilled in vacuo (10^{-1} torr). The fraction distilling at 40–100°C was collected. The residue was dissolved in benzene and evaporated as a thin film on a KBr window for the IR spectrum measurement. The distillate was redistilled under the same conditions to give the crude product II. The yields and compositions of the crude products are given in Table 1. The compounds are characterized by the mass spectra in abbreviated form, infrared spectra of the "finger print" region 1200–840 and 740–400 cm^{-1}, omitting the region of characteristic vibrations of the trimethylsilyl group, and ^{1}H, ^{13}C and ^{29}Si NMR spectra (CDCl$_3$ solution, δ scale, ppm).

1,2-Bis(trimethylsilyl)cyclohexa-1,4-diene (IIa). MS m/z (rel. intensity): 224(3.3; M), 209(12.1), 193(1.5), 175(0.7), 155(43.8), 151(7.4), 150(4.9), 136(29.2), 135(56.3), 121(14.6), 105(2.7), 74(13.2), 73(100), 59(8.9), 58(22.9), 54(1.2), 45(20.8), 43(11.1); IR (neat): 1119, 1073, 1030, 983, 897, 673, 639, 614 cm^{-1}; ^{1}H NMR: δ 0.25s, 2.82d (J 1.5 Hz), 5.82br s ppm (rel. int. 9/2/1); ^{13}C NMR: δ 1.30q, 32.0t, 124.8d, 146.2s ppm; ^{29}Si NMR: δ -7.14 ppm.

1,2-Bis(trimethylsilyl)-4-methylcyclohexa-1,4-diene (IIb). MS m/z (rel. intensity): 238(2.5; M), 223(6.9), 165(4.2), 164(10.4), 155(25.6), 151(5.1), 150(25.6), 149(51.0), 135(28.2), 121(2.7), 105(1.6), 97(4.0), 74(10.0), 73(100), 72(2.9), 68(9.1), 59(9.4), 58(10.0), 45(16.0), 43(7.4); IR (neat): 1169, 1036, 1004, 955, 906, 688, 680, 646, 639, 609, 555 cm^{-1}; ^{1}H NMR: δ 0.18s (18H), 1.65s (3H), 2.72mt (4H), 5.45brs ppm (1H); ^{13}C NMR: δ 1.30q, 23.0q, 33.5t, 36.9t, 118.5d, 131.3s, 145.8s ppm (2C); ^{29}Si NMR: δ -7.08, -7.32 ppm.

1,2-Bis(trimethylsilyl)-3-methylcyclohexa-1,4-diene (IIc). MS m/z (rel. intensity): 238(3.4; M), 223(6.6), 191(1.1), 165(4.9), 164(5.7), 155(26.1), 151(4.0), 150(14.2), 149(32.0), 135(39.1), 121(4.0), 105(3.8), 97(6.0), 74(12.0), 73(100), 72(4.2), 68(47.8), 59(13.0), 58(9.6), 53(4.0), 45(28.3), 43(15,2); IR (neat): 1177, 1124, 1071, 1041, 1024, 988, 963, 944, 917, 706, 693, 678, 646, 616, 550 484, 420 cm^{-1}; ^{1}H NMR: δ 0.19s (9H), 0.21s (9H), 0.96d (J 6.8 Hz, 3H), 2.74mt (2H), 3.04mt (1H), 5.50dd ppm (J 9.3 and 2.4 Hz, 1H); ^{13}C NMR: δ 1.2q, 2.2q, 21.7q, 32.2t, 35.1d, 124.2d, 132.0d, 146.3s, 153.0s ppm; ^{29}Si NMR: δ -6.88, -7.35 ppm.

1,2-Bis(trimethylsilyl)-4,5-dimethylcyclohexa-1,4-diene (IId). MS m/z (rel. intensity): 252(3.0; M), 237(6.2), 179(6.0), 178(13.2), 164(25.6), 163(66.7), 155(17.8), 149(31.0), 135(2.7), 82(15.6), 74(11.0), 73(100), 72(3.9), 67(9.1), 59(13.5), 58(6.0), 45(17.9), 43(7.5); IR (neat): 1154, 1138, 1060, 1011, 966, 941, 902, 695, 651, 639, 566, 459 cm^{-1}; ^{1}H NMR: δ 0.18s, 1.63s, 2.68brs ppm (rel. int. 9/3/2); ^{13}C NMR: δ 1.3q, 18.1q, 39.3t, 123.2s, 146.5s ppm; ^{29}Si NMR: δ -7.70 ppm.

1,2-Bis(triethylsilyl)-3,6-dimethylcyclohexa-1,4-diene (IIe). MS m/z (rel. intensity): 252(3.0; M), 237(4.3), 191(2.6), 179(4.3), 178(3.9), 169(1.3), 164(5.7), 163(18.7), 155(18.3), 149(4.5), 135(55.0), 82(19.1), 74(10.0), 73(100), 72(1.3), 67(11.7), 59(8.3), 45(15.7), 43(6.5); IR (neat): 1039, 1013, 972, 924, 678, 630, 618, 549, 509, 429 cm^{-1}; ^{1}H NMR: δ 0.16s, 0.86d (J 7.3 Hz), 2.72mt, 5.84mt ppm (rel. intensity 9/3/1/1); ^{13}C NMR: δ 1.2, 28.9, 41.5, 128.3, 144.5 ppm.

Dehydrogenation of 1,4-cyclohexadiene derivatives IIa–IId

About 0.5 g of II was degassed under freezing-thawing cycles in a 60 ml glass ampoule which was then sealed off and heated to 240°C for 2 h. After cooling to room temperature it was opened through a breakseal to vacuum line. Hydrogen (less than atmospheric pressure) was released and the 1,2-bis(trimethylsilyl)benzene derivative III was distilled into a trap to give about 0.45 g (90% yield). The purity of III was often better than that of II because the olefinic impurities partially polymerized out. The compounds IIIa–IIId are characterized by the same spectroscopic methods and in the same extent as their precursors IIa–IId.

1,2-Bis(trimethylsilyl)benzene (IIIa). MS m/z (rel. intensity) 222(14.0; M), 207(92.0), 191(100), 175(13.2), 163(3.1), 145(4.8), 135(3.2), 134(5.1), 119(7.6), 88(9.0), 74(4.9), 73(45.0), 59(4.5), 45(15.0), 43(8.0); IR (neat): 1119, 1055, 1039, 735, 691, 681, 659, 621, 438 cm^{-1}; ^{1}H NMR: δ 0.37s (18H), 7.28 and 7.68mt ppm (AA′BB′, 4H); ^{13}C NMR: δ 2.0q, 127.7d, 135.2d, 145.9s ppm ^{29}Si NMR: δ -3.37 ppm.

1,2-Bis(trimethylsilyl)-4-methylbenzene (IIIb). MS m/z (rel. intensity) 236(17.6; M), 221(95.0), 205(100), 189(4.8), 177(2.6), 175(2.1), 163(1.1), 161(1.5), 159(3.7), 150(1.8), 149(10.0), 148(3.0), 145(2.8), 133(5.4), 119(3.1), 105(2.6), 103(3.9), 95(10.2), 74(3.0), 73(52.0), 59(3.3), 45(12.0), 43(5.0); IR (neat): 1147, 1106, 1047, 876, 688, 678, 645, 624, 530, 440 cm^{-1}; ^{1}H NMR: δ 0.35s (18H), 2.32s (3H), 7.12dd (J 7.3 and 2.0 Hz), 7.48d (J 2.0 Hz), 7.56d ppm (J 7.3 Hz); ^{13}C NMR: δ 2.08 Qmt (^{1}J 118.4 Hz, ^{3}J 1.2 Hz), 21.4 Qt (^{1}J 126.3 Hz, ^{3}J 4.3 Hz), 128.7 Ddq (^{1}J 156.9 Hz, ^{3}J 4.9 Hz), 135.4 D (^{1}J 155.5 Hz), 136.2 Ddq (^{1}J 153.2 Hz, ^{3}J 4.9 Hz), 137.2s (^{3}J 6.1 Hz), 142.3s, 145.9s ppm; ^{29}Si NMR: δ -3.53, -3.65 ppm.

1,2-Bis(trimethylsilyl)-3-methylbenzene (IIIc). MS m/z (rel. intensity) 236(22.0; M), 221(93.0), 205(100), 189(5.4), 177(3.0), 175(3.0), 163(4.5), 162(5.0), 159(4.3), 149(28.0), 148(32.5), 145(6.4), 133(53.0), 121(4.0), 119(4.5), 105(5.5), 95(12.5), 74(7.0), 73(89.0), 59(6.9), 45(25.0), 43(9.5); IR (neat): 1187, 1145, 1055, 865, 720, 693, 679, 638, 622, 445 cm^{-1}; ^{1}H NMR: δ 0.37s (9H), 0.42s (9H), 2.49s (3H), 7.03–7.59mt ppm (ABC, 3H); ^{13}C NMR: δ 3.1 Q(^{1}J 120.9 Hz), 3.8 Q (^{1}J 119.6 Hz), 25.1 Qd (^{1}J 128.2 Hz, ^{3}J 4.9 Hz), 127.2 D (^{1}J 157.8 Hz, H(5)), 130.7 Ddq (^{1}J 156.3 Hz, ^{3}J 6.1 Hz, H(4)), 133.1 Dd (^{1}J 156.3 Hz, ^{3}J 7.3 Hz, H(6)), 144.2s, 145.3s, 147.1s; ^{29}Si NMR: δ -2.93, -5.70 ppm.

1,2-Bis(trimethylsilyl)-4,5-dimethylbenzene (IIId). Solid, m.p. 43–44°C: MS m/z (rel. intensity): 250(24.0; M), 235(93.5), 219(100), 205(4.2), 204(5.4), 191(3.1), 189(2.4), 173(4.3), 163(19.6), 161(4.9), 159(6.2), 147(9.1), 145(5.4), 135(4.0), 133(3.8), 131(3.9), 129(4.8), 119(4.7), 110(6.2), 102(13.0), 83(2.6), 74(5.0), 73(52.0), 65(2.0), 59(9.0), 57(4.5), 45(22.0), 43(11.5); IR (neat): 1133, 1017, 1006, 940, 690, 681, 666, 635, 615, 569, 480, 442 cm^{-1}; ^{1}H NMR: δ 0.34s (18H), 2.25s (6H), 7.42s (2H); ^{13}C NMR: δ 2.08Q (^{1}J 152.6 Hz), 19.6Qd (^{1}J 125.7 Hz, ^{3}J 4.9 Hz), 136.2s, 137.1Dq (^{1}J 152.6 Hz, ^{3}J 4.9 Hz), 143.1s; ^{29}Si NMR δ -4.01 ppm.

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