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Pd(0)-Catalysed Coupling of Cyclopropenylzinc Chlorides and Cyclopropenylstannanes – A New Efficient Synthesis of 1-Phenyl-, 1-Ethenyl-, and 1-Ethynyl-1-cyclopropenes☆

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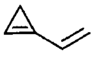
[3,3-Dimethyl-2-(trimethylsilyl)-1-cyclopropen-1-yl]zinc chloride (**4**) reacts with haloarenes and -alkenes as well as 1-bromoacetylenes under Pd(0) catalysis to give the corresponding 1-phenyl-, 1-ethenyl-, and 1-ethynyl-1-cyclopropenes **6** in isolated yields ranging from 47 to 99%. The corresponding 1-cyclopropen-1-ylstannane **5** reacts with haloarenes only at higher temperatures, and the yields range from 10 to 98%, depending on the substrate and reaction conditions.

In the context of our continuing interest in thermal ring-opening reactions of substituted cyclopropenes[2], we were in need of an efficient route to cyclopropenes bearing phenyl, ethenyl, and ethynyl substituents in 1- or 2-position of the cyclopropene ring. These substituents are known to cause substantial stabilisations of α-radical or α-carbene centers[3] of the most probable intermediates in the isomerisation of cyclopropenes.

Although 1- or 2-phenyl-1-cyclopropenes are well-known compounds, they are not stable at room temperature unless they are tetrasubstituted[4]. In contrast, very few examples of 1- and 2-ethenyl- and -ethynyl-1-cyclopropenes are mentioned in the literature[5,6]. The parent compound 1-ethenyl-1-cyclopropene (**1**) dimerises in a [2 + 2] cycloaddition at −60°C to give 1,2-diethenyl-*anti*-tricyclo[3.1.0.0^{2,4}]hexane[5]. Only one year ago the first example of a 1-ethynyl-1-cyclopropene, the highly stabilised diphenyl-substituted **2**, was isolated in an overall yield of 10% upon photolysis of the corresponding 3*H*-pyrazole[6].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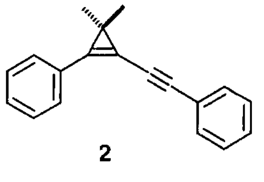
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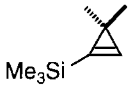

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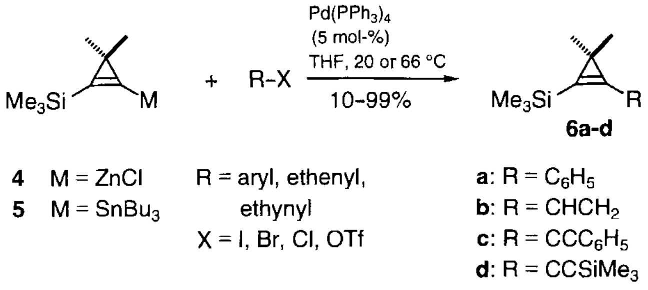
For our planned gas-phase kinetic studies considerable amounts (gram scale) of such cyclopropenes were required. In addition, the compounds had to be reasonably stable at room temperature. Because of our previous experience with trimethylsilyl-substituted cyclopropenes[2b,c] we envisaged derivatives of 3,3-dimethyl-1-(trimethylsilyl)-1-cyclopropene (**3**) as model compounds for this study.

The Pd(0)-catalysed coupling reactions of ethynylzinc chlorides[7] and ethynylstannanes[8] with haloalkenes and ethenyl triflates as well as haloarenes and phenyl triflates have found widespread application in organic synthesis. According to the similar C−H acidities of cyclopropenes and acetylenes[9] we turned our attention to the coupling reactions of zinc- and tin-substituted cyclopropenes under similar conditions (Scheme 1).

Scheme 1. (For more details see Table 1)



The metallated cyclopropenes **4** and **5** were easily prepared in excellent yields by treating lithiated 3,3-dimethyl-1-(trimethylsilyl)-1-cyclopropene (**3**)[2b] with dry zinc chloride or tributyltin chloride. While the cyclopropenylzinc chloride **4** was not isolated, but used as a solution in tetrahydrofuran (THF), the stannane **5** was isolated in pure form by column chromatography. In the absence of oxygen it was stable at room temperature for months[10]. Compounds **4** and **5** were allowed to react at different temperatures under standardised conditions, i.e. with one equivalent of substrate (e.g. haloarene) and 5 mol % of tetrakis(triphenylphosphane)palladium(0) [Pd(PPh_3)$_4$] in THF. While **4** reacted at room temperature within 24 h, the reaction of **5**

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generally required higher temperatures (refluxing THF) to give the 1-substituted 2-(trimethylsilyl)cyclopropenes **6**.

Table 1. 1-Substituted 3,3-dimethyl-2-(trimethylsilyl)-1-cyclopropenes **6a–d** from cyclopropenylzinc chloride **4** and cyclopropenylstannane **5**

Entry	Starting Materials		X	Reaction Temp. [°C]	Product	Yield (%)[a]
		R				
1	**4**[b]	C_6H_5	I	20	**6a**	99
2	**4**	C_6H_5	Br	20	**6a**	65
3	**4**	C_6H_5	Cl	20	**6a**	0
4	**4**	$CHCH_2$	I	20	**6b**	80
5	**4**	CCC_6H_5	Br	20	**6c**	72
6	**4**	$CCSiMe_3$	Br	20	**6d**	49
7	**5**	CCC_6H_5	I	20	**6c**	0
8	**5**	$CCSiMe_3$	I	20	**6d**	0
9	**5**	C_6H_5	I	66	**6a**	98
10	**5**	C_6H_5	Br	66	**6a**	63
11	**5**	C_6H_5	Cl	66	**6a**	0
12	**5**	C_6H_5	OTf	66	**6a**	10
13	**5**	C_6H_5	OTf[c]	66	**6a**	37
14	**5**	$CHCH_2$	I	66	**6b**	0
15	**5**	$CHCH_2$	Br	66	**6b**	0
16	**5**	CCC_6H_5	I	66	**6c**	0
17	**5**	CCC_6H_5	Br	66	**6c**	0

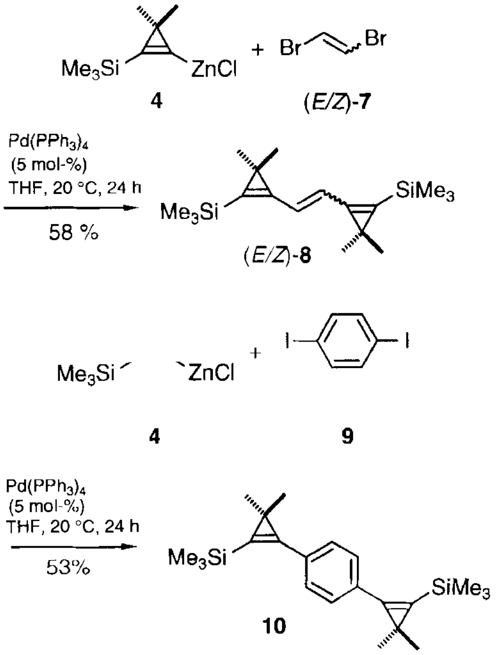
[a] Isolated yield. – [b] Generated in situ. – [c] Three equivalents of dry LiCl was added.

The yields depend strongly on the leaving group ability of the substituent X in the coupling reagent R–X (see Table 1). The reaction of cyclopropenylzinc chloride **4** with phenyl iodide gave the desired 1-phenylcyclopropene **6a** in an isolated yield of 99%, while the reaction with phenyl bromide only afforded 65%, and phenyl chloride did not react at all. The reaction with ethenyl iodide furnished the 1-ethenyl-3,3-dimethylcyclopropene **6b** in an isolated yield of 80%. Only 1-bromoacetylenes reacted with **4** to yield the desired 1-ethynylcyclopropenes **6c** and **6d**, while 1-iodoacetylenes did not couple with **4**, but formed the corresponding butadiynes in low yields. The fast homocoupling reaction must obviously be accompanied by an oxidation of the Pd(0) catalyst.

The reaction of tin-substituted cyclopropene **5** in refluxing THF with phenyl iodide and bromide gave 1-phenylcyclopropene **6a** in 98 and 63% yield, respectively. Again phenyl chloride did not react at all. Phenyl triflate, known to have a highly activated C–O bond for the insertion of the Pd(0) catalyst[11], afforded a surprisingly low yield (10%) of **6a**. In the presence of three equivalents of dry lithium chloride[12], the isolated yield of **6a** increased to 37% (see Table 1). Surprisingly, neither ethenyl nor phenylethynyl bromide or iodide yielded any of the coupling products **6b** or **6c**, respectively, when reacted with the stannane **5**.

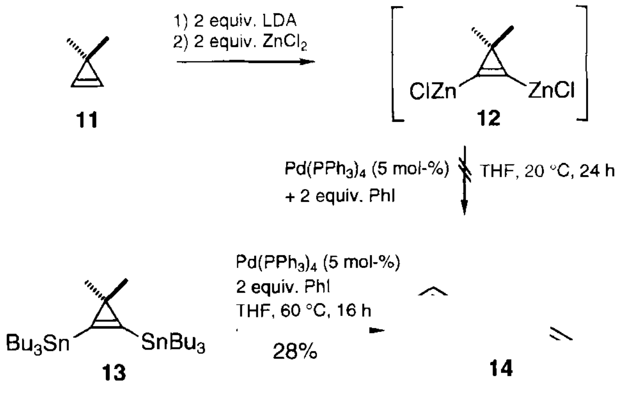
Even twofold coupling reactions with dihaloalkenes and dihaloarenes are possible (see Scheme 2). They were carried out by using two equivalents of either **4** or **5** and one equivalent of the substrate according to the reaction stoichiometry. The commercially available mixture of (*E*)- and (*Z*)-1,2-dibromoethene [(*E*/*Z*)-**7**] (*E*/*Z* = 38:62) gave a mixture of (*E*)- and (*Z*)-1,2-bis[3,3-dimethyl-2-(trimethylsilyl)-1-cyclopropen-1-yl]ethene [(*E*/*Z*)-**8**] in 58% yield (*E*/*Z* = 87:13); apparently, the (*E*) and (*Z*) isomer of **7** react with approximately the same rate, and both give predominantly the (*E*)-configurated coupling product[13]. The assignment of diastereomers was made by way of the ^3J coupling constants which are visible in the ^{13}C satellites of the olefinic proton signals. Similarly, *p*-bis[3,3-dimethyl-2-(trimethylsilyl)-1-cyclopropen-1-yl)benzene (**10**) was obtained from **4** and *p*-diiodobenzene (**9**) in 53% yield.

Scheme 2



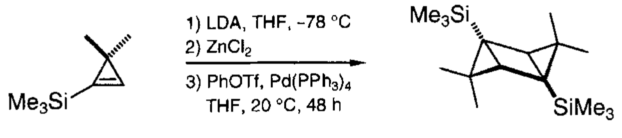
On the other hand, an attempted coupling reaction of 1,2-bis(chlorozincio)-3,3-dimethyl-1-cyclopropene (**12**), generated from 3,3-dimethyl-1-cyclopropene (**11**) with two equivalents each of LDA and zinc chloride, failed; it is unclear, whether this was due to a failure of forming the difunctional derivative **12** or whether **12** was not stable, even under the relatively mild reaction conditions (room temperature). But bis(tributylstannyl)cyclopropene **13**[2b] could be coupled with two equivalents of phenyl iodide (Scheme 3) to give the expected 3,3-dimethyl-1,2-diphenyl-1-cyclopropene (**14**) in a modest yield of 28%.

Scheme 3



Surprisingly, when phenyl triflate was treated with the cyclopropenylzinc chloride **4** under the same conditions as phenyl iodide and bromide, no coupling product **6a** could be isolated. Instead, the [2 + 2] dimer of **3**, 3,3,6,6-tetramethyl-1,4-bis(trimethylsilyl)tricyclo[$3.1.0.0^{2,4}$]hexane (**15**), was obtained in 68% yield (Scheme 4). The same product formed more slowly without added phenyl triflate, but not at all without first deprotonating the cyclopropene **3**. This result deviates from an earlier observation of a Pd(II)-catalysed dimerisation of 1-methyl-1-cyclopropene[14]. The 1,4-positioning of the two trimethylsilyl groups in the dimer **15** was not rigorously proved, but assumed to be the most probable for steric reasons, as the Pd(II)-catalysed dimerisation of 1-methyl-1-cyclopropene led to a mixture of 1,2- and 1,4-dimethyltricyclohexanes[14].

Scheme 4



3 68% **15**

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Experimental

Melting points (uncorrected): Büchi melting point apparatus. – ^1H NMR: Bruker AW 250; $\delta(CHCl_3) = 7.26$, $\delta(SiMe_4) = 0.00$. – ^{13}C NMR: Bruker AW 250; 62.9 MHz, $\delta(CDCl_3) = 77.0$, multiplicities determined by DEPT. – Flash liquid chromatography: Silica gel (SDS 60 ACC 230–400 mesh) or Merck Kieselgel 60 (200–400 mesh)[15]. – All reactions were carried out in an inert gas atmosphere and monitored by TLC (UV detection) on aluminium sheets coated with Silica 60 F_{254} (Merck).

3,3-Dimethyl-1-(trimethylsilyl)-1-cyclopropene (**3**) was prepared according to a procedure of Baird et al.[16]. 3,3-Dimethyl-1-(tributylstannyl)-2-(trimethylsilyl)-1-cyclopropene (**5**) was prepared by following a procedure of de Meijere et al.[2b]. Dry zinc chloride was obtained by refluxing commercially available $ZnCl_2$ with $SOCl_2$ for 24 h in a slow stream of N_2 followed by filtration in an inert gas atmosphere. Tetrakis(triphenylphosphane)palladium was prepared according to the method of Coulson[17]. 1-Bromo-2-phenylacetylene was obtained by following a procedure of Miller et al.[18], while 1-bromo-2-(trimethylsilyl)acetylene was prepared according to a procedure of Eastmond and Walton[19]. The 1-iodoacetylenes were prepared by deprotonation of the corresponding acetylenes with *n*BuLi in THF and consecutive quenching with iodine at temperatures lower than −100°C[20].

2-Phenyl-, 2-Ethenyl-, and 2-Ethynyl-Substituted 3,3-Dimethyl-1-(trimethylsilyl)cyclopropenes from [3,3-Dimethyl-1-(trimethylsilyl)-1-cyclopropen-1-yl]zinc Chloride (**4**). – *General Procedure (GP 1):* 3,3-Dimethyl-1-(trimethylsilyl)-1-cyclopropene (**3**, 1.69 g, 12.02 mmol) was added to a solution of 2.36 M *n*-butyllithium in hexane (5.10 ml, 12.0 mmol) and diisopropylamine (1.70 ml, 12.0 mmol) in dry THF (50 ml) at −78°C. The solution was stirred at 20°C for 30 min, cooled again to −78°C, and $ZnCl_2$ (2.46 g, 18.0 mmol) was added. After an additional 30 min at room temp., the resulting suspension was added to a solution of $Pd(PPh_3)_4$ (690 mg, 5 mol %) and 12.0 mmol of the respective aryl, alkenyl, or alkynyl halide in dry THF (25 ml) in a Pyrex screw bottle equipped with a gas inlet. The mixture was stirred for 24 h, added to pentane (100 ml), filtered, and the filtrate was concentrated under reduced pressure. The residue was purified by flash chromatography or kugelrohr (bulb-to-bulb) distillation.

2-Phenyl-, 2-Ethenyl-, and 2-Ethynyl-Substituted 3,3-Dimethyl-1-(trimethylsilyl)cyclopropenes from 3,3-Dimethyl-1-(tributylstannyl)-2-(trimethylsilyl)-1-cyclopropene (**5**). – *General Procedure (GP 2):* Compound **5** (400 mg, 0.92 mmol) was added to a solution of 0.92 mmol of the respective aryl, alkenyl, or alkynyl halide or aryl triflate and $Pd(PPh_3)_4$ (53 mg, 0.046 mmol, 5 mol %) in dry THF (20 ml). The resulting suspension was heated under reflux for 24 h, added to pentane (50 ml), filtered, and the filtrate was concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel (40 g) (eluent pentane).

3,3-Dimethyl-1-phenyl-2-(trimethylsilyl)-1-cyclopropene (**6a**)

a) According to GP 1 1.30 g (9.27 mmol) of the 3,3-dimethylcyclopropene **3** and 1.03 ml (9.24 mmol) of idobenzene gave, after kugelrohr distillation, 1.98 g (99%) of **6a**, b.p. 120°C/0.01 mbar. For gas-phase kinetic experiments[21] a sample was purified to >99% by preparative-scale gas chromatography. – IR (film): $\tilde{\nu}$ = 3078 cm^{-1} ($C-H_{arom.}$), 2958 (C–H), 1755, 1596 (C=C), 1248 ($Si-CH_3$). – ^1H NMR (250 MHz, $CDCl_3$): δ = 0.32 [s, 9H, $Si(CH_3)_3$], 1.38 (s, 6H, CH_3), 7.29–7.38 (m, 1H, Ar-H), 7.39–7.48 (m, 2H, Ar-H), 7.50–7.57 (m, 2H, Ar-H). – ^{13}C NMR (62.9 MHz, $CDCl_3$, DEPT): δ = −0.39 [+, $Si(CH_3)_3$], 20.32 (C_{quat}, C-3), 26.95 (+, CH_3), 126.02 (C_{quat}, C-1), 128.30 (+, C-4′), 128.61 [+, C-2′(6′) or C-3′(5′)], 128.69 [+, C-3′(5′) or C-2′(6′)], 130.97 (C_{quat}, C-1′), 144.61 (C_{quat}, C-2). – MS (70 eV), *m/z* (%): 216 (8) [M^+], 201 (4) [$M^+ - CH_3$], 159 (6), 143 (5) [$M^+ - Si(CH_3)_3$], 128 (8) [$M^+ - CH_3 - Si(CH_3)_3$], 77 (5) [$C_6H_5^+$], 73 (100) [$Si(CH_3)_3^+$], 45 (9). – $C_{14}H_{20}Si$ (216.4): calcd. C 77.71, H 9.31; found C 77.77, H 9.21.

b) According to GP 2 **5** was treated each with 208 mg (0.92 mmol) of phenyl triflate, 191 mg (0.508 mmol) of phenyl nonaflate, 104 mg (0.92 mmol) of chlorobenzene, 97 µl (0.92 mmol) of bromobenzene, and 188 mg (0.92 mmol) of iodobenzene, respectively. After chromatographic separation (40 g of silica gel, elution with light petroleum, boiling range 50–70°C, R_f = 0.62) a yield of 10% (triflate, 37% upon addition of 3 equiv. of LiCl), 0% (nonaflate), 0% (chloride), 63% (bromide), and 98% (iodide) of **6a** was obtained.

1-Ethenyl-3,3-dimethyl-2-(trimethylsilyl)-1-cyclopropene (**6b**): According to GP 1 1.69 g (12.0 mmol) of **3** was treated with 2.54 ml (26.7 mmol) of iodoethene. After kugelrohr distillation 1.60 g (80%) of **6b** was obtained as a colourless liquid, b.p. 20°C/0.01 mbar. – IR (film): $\tilde{\nu}$ = 2959 cm^{-1} (C–H), 1751, 1593 (C=C), 1248 ($Si-CH_3$). – ^1H NMR (250 MHz, $CDCl_3$): δ = 0.21 [s, 9H, $Si(CH_3)_3$], 1.23 (s, 6H, CH_3), 5.47 (dd, ^3J = 16.9, ^2J = 2.4 Hz, 1H, ethenyl-H), 5.51 (dd, ^3J = 10.3, ^2J = 2.4 Hz, 1H, ethenyl-H), 6.60 (dd, ^3J = 16.9, ^3J = 10.3 Hz, 1H, ethenyl-H). – ^{13}C NMR (62.9 MHz, $CDCl_3$, DEPT): δ = −0.64 [+, $Si(CH_3)_3$], 20.15 (C_{quat}, C-3), 26.72 (+, CH_3), 121.11 (−, C-2′), 125.99 (+, C-1′), 128.99 (C_{quat}, C-1), 143.82 (C_{quat}, C-2). – MS (70 eV), *m/z* (%): 166 (3) [M^+], 151 (9) [$M^+ - CH_3$], 139 (41) [$M^+ - C_2H_3$], 124 (23) [$M^+ - CH_3 - C_2H_3$], 73 (100) [$SiMe_3^+$], 45 (17), 43 (28). – $C_{10}H_{18}Si$: calcd. 166.1178, found 166.1177 (MS).

3,3-Dimethyl-1-(2-phenylethynyl)-2-(trimethylsilyl)-1-cyclopropene (**6c**): According to GP 1 233 mg (1.66 mmol) of **3** and 300 mg (1.66 mmol) of 1-bromo-2-phenylacetylene gave, after column chromatography (50 g of silica gel, elution with pentane, R_f = 0.48), 286 mg (72%) of **6c** as a colourless oil. – IR (film): $\tilde{\nu}$ = 3063 cm^{-1} (C–H$_{arom}$), 2960, 2190 (C≡C), 1488, 1442 (ω-Ph), 1249 (Si–CH$_3$). – ^{1}H NMR (250 MHz, CDCl$_3$): δ = 0.22 [s, 9H, Si(CH$_3$)$_3$], 1.23 (s, 6H, CH$_3$), 7.26–7.59 (m, 5H, Ar-H). – ^{13}C NMR (62.9 MHz, CDCl$_3$, DEPT): δ = −1.04 [+, Si(CH$_3$)$_3$], 24.42 (C$_{quat}$, C-3), 27.29 (+, CH$_3$), 80.43 (C$_{quat}$, C-1'), 105.65 (C$_{quat}$, C-2'), 123.30 (C$_{quat}$, C-1), 128.30 [+, C-3''(5'')], 128.47 (+, C-4''), 129.84 (C$_{quat}$, C-2), 131.46 [+, C-2''(6'')], 131.99 (C$_{quat}$, C-1''). – MS (70 eV), *m/z* (%): 240 (38) [M$^+$], 225 (6) [M$^+$ − CH$_3$], 180 (10), 167 (4) [M$^+$ − SiMe$_3$], 101 (8) [PhC≡C$^+$], 73 (100) [SiMe$_3^+$], 59 (4), 45 (9). – C$_{16}$H$_{20}$Si (240.4): calcd. C 79.93, H 8.39; found C 79.99, H 8.51.

3,3-Dimethyl-1-(trimethylsilyl)-2-[2-(trimethylsilyl)ethynyl]-1-cyclopropene (**6d**): According to GP 1 395 mg (2.82 mmol) of **3** was treated with 500 mg (2.82 mmol) of 1-bromo-2-(trimethylsilyl)acetylene. After column chromatography (70 g of silica gel, elution with pentane, R_f = 0.67) 328 mg (49%) of **6d** was obtained as a colourless oil. – IR (film): $\tilde{\nu}$ = 2940 cm^{-1} (C–H), 2900, 2850, 2120 (C≡C), 1720 (C=C), 1250 (Si–CH$_3$). – ^{1}H NMR (250 MHz, CDCl$_3$): δ = 0.18 [s, 9H, Si(CH$_3$)$_3$], 0.24 [s, 9H, Si(CH$_3$)$_3$], 1.20 (s, 6H, CH$_3$). – ^{13}C NMR (62.9 MHz, CDCl$_3$, DEPT): δ = −1.13 [+, Si(CH$_3$)$_3$], −0.09 [+, Si(CH$_3$)$_3$], 24.71 (C$_{quat}$, C-3), 27.17 (+, CH$_3$), 95.39 (C$_{quat}$, C-2'), 112.43 (C$_{quat}$, C-1'), 130.21 (C$_{quat}$, C-1), 140.95 (C$_{quat}$, C-2). – MS (70 eV), *m/z* (%): 236 (90) [M$^+$], 221 (20) [M$^+$ − CH$_3$], 179 (87), 148 (98) [M$^+$ − CH$_3$ − SiMe$_3$], 97 (48) [Me$_3$SiC$_2^+$], 73 (100) [SiMe$_3^+$], 45 (56). – C$_{13}$H$_{24}$Si$_2$: calcd. 236.1417, found 236.1417 ± 0.0002 (MS).

1,2-Bis[3,3-dimethyl-2-(trimethylsilyl)-1-cyclopropen-1-yl]ethene [(*E*/*Z*)-**8**]: According to GP 1 368 mg (2.63 mmol) of **3** was treated with 244 mg (1.31 mmol) of (*E*/*Z*)-1,2-dibromoethene (*E*/*Z* = 38:62). The chromatographic separation (50 g of silica gel, elution with pentane, R_f = 0.65) gave 232 mg (58%) of (*E*/*Z*)-**8** as a light yellow oil. – IR (film): $\tilde{\nu}$ = 2957 cm^{-1} (C–H), 1753, 1694 (C=C), 1247 (Si–CH$_3$). – ^{1}H NMR (250 MHz, CDCl$_3$), (*E*)-**8** (87%): δ = 0.20 [s, 18H, Si(CH$_3$)$_3$], 1.31 (s, 12H, CH$_3$), 6.63 [s, 2H, 1(2)-H]. – (*Z*)-**8** (13%): δ = 0.09 [s, 18H, Si(CH$_3$)$_3$], 1.29 (s, 12H, CH$_3$), 6.45 [s, 2H, 1(2)-H]. – ^{13}C NMR [62.9 MHz, CDCl$_3$, DEPT, only (*E*)-**8**]: δ = −0.56 [+, Si(CH$_3$)$_3$], 20.57 (C$_{quat}$, C-3'), 26.84 (+, CH$_3$), 124.19 [+, C-1(2)], 132.72 (C$_{quat}$, C-1'), 142.75 (C$_{quat}$, C-2'). – MS (70 eV), *m/z* (%): 304 (4) [M$^+$], 289 (7) [M$^+$ − CH$_3$], 231 (9) [M$^+$ − SiMe$_3$], 216 (14) [M$^+$ − CH$_3$ − SiMe$_3$], 201 (41) [M$^+$ − SiMe$_3$ − 2 CH$_3$], 110 (22), 73 (100) [SiMe$_3^+$], 59 (10), 41 (15). – C$_{18}$H$_{32}$Si$_2$ (304.6): calcd. C 70.97, H 10.59; found C 71.08, H 10.59.

1,4-Bis[3,3-dimethyl-2-(trimethylsilyl)-1-cyclopropen-1-yl]benzene (**10**): According to GP 1 356 mg (2.54 mmol) of **3** and 279 mg (0.85 mmol) of 1,4-diiodobenzene gave, after column chromatography (50 g of silica gel, elution with petroleum ether, boiling range 50–70°C) 2 fractions. – I: 158 mg (53%) of **10**, colourless solid, m.p. 58°C, R_f = 0.68. – IR (KBr): $\tilde{\nu}$ = 2957 cm^{-1}, 2854 (C–H), 1692, 1603 (C=C), 1248 (Si–CH$_3$). – ^{1}H NMR (250 MHz, CDCl$_3$): δ = 0.29 [s, 18H, Si(CH$_3$)$_3$], 1.31 (s, 12H, CH$_3$), 7.49 (s, 4H, Ar-H). – ^{13}C NMR (62.9 MHz, CDCl$_3$, DEPT): δ = −0.40 [+, Si(CH$_3$)$_3$], 20.47 (C$_{quat}$, C-3'), 26.90 (+, CH$_3$), 127.28 (C$_{quat}$, C-1'), 128.90 [+, C-2(3,5,6)], 130.76 [C$_{quat}$, C-1(4)], 144.28 (C$_{quat}$, C-2'). – MS (70 eV), *m/z* (%): 354 (21) [M$^+$], 339 (6) [M$^+$ − CH$_3$], 281 (15) [M$^+$ − SiMe$_3$], 266 (21) [M$^+$ − CH$_3$ − SiMe$_3$], 224 (28), 97 (7), 73 (100) [SiMe$_3^+$], 59 (5), 45 (12). – C$_{22}$H$_{34}$Si$_2$: calcd. 354.2199, found 354.2199 ± 0.0002 (MS).

II: 36 mg (20%) of a compound proposed as 4,4'-bis[3,3-dimethyl-2-(trimethylsilyl)-1-cyclopropen-1-yl]biphenyl, colourless solid, m.p. 79°C, R_f = 0.49. – ^{1}H NMR (250 MHz, CDCl$_3$): δ = 0.29 [s, 18H, Si(CH$_3$)$_3$], 1.35 (s, 12H, CH$_3$), 7.57 (AA' part of an AA'BB' system, ^3J = 9.5 Hz, 4H, Ar-H), 7.66 (BB' part of an AA'BB' system, ^3J = 9.5 Hz, 4H, Ar-H). – ^{13}C NMR (62.9 MHz, CDCl$_3$, DEPT): δ = −0.37 [+, Si(CH$_3$)$_3$], 20.40 (C$_{quat}$, C-3''), 26.96 (+, CH$_3$), 126.86 (C$_{quat}$, C-1''), 127.24 [+, C-3(3',5,5')], 129.00 [+, C-2(2',6,6')], 130.11 [C$_{quat}$, C-4(4')], 140.57 [C$_{quat}$, C-1(1')], 144.08 (C$_{quat}$, C-2''). – MS (70 eV), *m/z* (%): 430 (16) [M$^+$], 357 (6) [M$^+$ − SiMe$_3$], 300 (12), 266 (8), 224 (8), 97 (14), 73 (100) [SiMe$_3^+$], 45 (18).

3,3-Dimethyl-1,2-diphenyl-1-cyclopropene (**14**): According to GP 2 550 mg (2.70 mmol) of iodobenzene and 880 mg (1.36 mmol) of 3,3-dimethyl-1,2-bis(tributylstannyl)-1-cyclopropene (**13**) gave, after chromatographic separation (40 g of silica gel, elution with pentane, R_f = 0.3), 85 mg (28%) of **14** as a white solid, m.p. 93°C. – IR (KBr): $\tilde{\nu}$ = 3077 cm^{-1} (C–H$_{arom}$), 2957, 2855 (C–H), 1805, 1596 (C=C). – ^{1}H NMR (250 MHz, CDCl$_3$): δ = 1.56 (s, 6H, CH$_3$), 7.31–7.43 (m, 2H, Ar-H), 7.45–7.54 (m, 4H, Ar-H), 7.60–7.73 (m, 4H, Ar-H). – ^{13}C NMR (62.9 MHz, CDCl$_3$, DEPT): δ = 20.32 (C$_{quat}$, C-3), 24.67 (+, CH$_3$), 124.22 [C$_{quat}$, C-1(2)], 127.99 (+, C-4'), 128.77 [+, C-3'(5')], 129.19 [+, C-2'(6')], 130.23 (C$_{quat}$, C-1'). – MS (70 eV), *m/z* (%): 220 (56) [M$^+$], 205 (100) [M$^+$ − CH$_3$], 178 (9), 170 (22), 142 (16) [M$^+$ − C$_6$H$_6$], 128 (14), 91 (10) [C$_7$H$_7^+$], 77 (8) [C$_6$H$_5^+$]. – C$_{17}$H$_{16}$: calcd. 220.1252, found 220.1252 ± 0.0002 (MS).

Reaction of 3,3-Dimethyl-1-(trimethylsilyl)-1-cyclopropene (**3**) *with Phenyl Triflate:* According to GP 1 190 mg (1.36 mmol) of **3** was treated with 200 mg (0.88 mmol) of phenyl triflate. Column chromatography (60 g of silica gel, elution with pentane, R_f = 0.69) yielded 129 mg (68%) of *3,3,6,6-tetramethyl-1,4-bis(trimethylsilyl)-tricyclo[3.1.0.0^{2,4}]hexane* (**15**) as a colourless solid, m.p. 56°C. – IR (KBr): $\tilde{\nu}$ = 2950 cm^{-1} (C–H), 1249 (Si–CH$_3$). – ^{1}H NMR (250 MHz, CDCl$_3$): δ = 0.08 [s, 18H, Si(CH$_3$)$_3$], 1.03 (s, 6H, CH$_3$), 1.38 (s, 6H, CH$_3$), 1.45 [s, 2H, 2(5)-H]. – ^{13}C NMR (62.9 MHz, CDCl$_3$, DEPT): δ = 1.25 [+, Si(CH$_3$)$_3$], 19.61 (+, CH$_3$), 24.03 (+, CH$_3$), 31.02 [C$_{quat}$, C-1(4)], 33.68 [+, C-2(5)], 40.98 [C$_{quat}$, C-3(6)]. – MS (70 eV), *m/z* (%): 280 (8) [M$^+$], 207 (14) [M$^+$ − SiMe$_3$], 192 (8) [M$^+$ − SiMe$_3$ − CH$_3$], 177 (18) [M$^+$ − SiMe$_3$ − 2 CH$_3$], 137 (16), 110 (62), 73 (100) [SiMe$_3^+$]. – C$_{16}$H$_{32}$Si$_2$ (280.6): calcd. C 68.49, H 11.49; found C 68.59, H 11.49.

☆ Dedicated to Professor *Christoph Rüchardt* on the occasion of his 65th birthday.

[1] Part 27: L. Hadjiarapoglou, A. de Meijere, H.-J. Seitz, I. Klein, D. Spitzner, *Tetrahedron Lett.* **1994**, in press; for Part 26 see: G. McGaffin, A. de Meijere, *Synthesis*, **1994**, in press.

[2] [2a] W. Weber, A. de Meijere, *Angew. Chem.* **1980**, *92*, 135–136; *Angew. Chem. Int. Ed. Engl.* **1980**, *19*, 138–140; R. R. Kostikov, A. de Meijere, *J. Chem. Soc., Chem. Commun.* **1984**, 1528–1529; W. Weber, A. de Meijere, *Chem. Ber.* **1985**, *118*, 2450–2471. – [2b] M. A. Kirms, H. Primke, M. Stohlmeier, A. de Meijere, *Recl. Trav. Chim. Pays-Bas* **1986**, *105*, 462–464. – [2c] R. Walsh, S. Untiedt, M. Stohlmeier, A. de Meijere, *Chem. Ber.* **1989**, *122*, 637–642. – [2d] R. Walsh, C. Wolf, S. Untiedt, A. de Meijere, *J. Chem. Soc., Chem. Commun.* **1992**, 421–422. – [2e] R. Walsh, C. Wolf, S. Untiedt, A. de Meijere, *J. Chem. Soc., Chem. Commun.* **1992**, 422–423. – [2f] R. Walsh, S. Untiedt, A. de Meijere, *Chem. Ber.* **1994**, *127*, 237–245.

[3] [3a] U. Misslitz, A. de Meijere in *Methoden Org. Chem. (Houben-Weyl)* **1989**, vol. E 19b, p. 664–769. – [3b] C. Wentrup in *Methoden Org. Chem. (Houben-Weyl)* **1989**, vol. E 19b, p. 824–999. – [3c] H. D. Hartzler in *Carbenes*, vol. II (Eds.: R. A. Moss, M. Jones, Jr.), Wiley, New York, **1975**, p. 43–100. – [3d] A. M. Trozzolo, E. Wasserman in *Carbenes*, vol. II (Eds.: R. A. Moss, M. Jones, Jr.), Wiley, New York, **1975**, p. 185–206.

[4] A. Padwa, K. E. Krumpe, L. W. Terry, M. W. Wannamaker, *J. Org. Chem.* **1989**, *54*, 1635–1642.

[5] W. E. Billups, L.-J. Lin, *Tetrahedron* **1986**, *42*, 1575–1579.

[6] M. A. Kuznetsov, Y. V. Dorofeeva, V. V. Semenovskii, V. A. Gindin, A. N. Studenikov, *Tetrahedron* **1992**, *48*, 1269–1280.

[7] A. Carpita, R. Rossi, *Tetrahedron Lett.* **1986**, *27*, 4351–4354; B. P. Andreini, A. Carpita, R. Rossi, *ibid.* **1986**, *27*, 5533–5534.

[8] [8a] S. Matsubara, M. Mitani, K. Utimoto, *Tetrahedron Lett.* **1987**, *28*, 5857–5860. – [8b] L. S. Liebeskind, J. Zhang, *J. Org. Chem.* **1991**, *56*, 6379–6385. – [8c] I. P. Beletskaya, *J. Organomet. Chem.* **1983**, *250*, 551–564.

[9] Cf.: K. B. Wiberg, W. J. Bartley, *J. Am. Chem. Soc.* **1960**, *82*, 6375–6380; G. L. Closs, L. E. Closs, *ibid.* **1961**, *83*, 1003–1004; **1963**, *85*, 99–104; A. J. Schipperijn, *Recl. Trav. Chim. Pays-Bas* **1971**, *90*, 1110–1112.

[10] During a gas-phase kinetic study 3,3-dimethyl-1-(tributylstannyl)-1-cyclopropene[2f] was stored in a vacuum line at room temperature over a period of two months without any sign of decomposition.

[11] [11a] S. Cacchi, E. Morera, G. Ortar, *Synthesis* **1986**, 320–322. – [11b] Q.-Y. Chen, Z.-Y. Yang, *Tetrahedron Lett.* **1986**, *27*,1171–1174. – [11c] Q.-Y. Chen, Y.-B. He, *Tetrahedron Lett.* **1987**, *28*, 2387–2388.

[12] The addition of lithium chloride to accelerate coupling reactions of alkenyl and aryl triflates has been suggested by: R. C. Larock, S. S. Hershberger, *J. Org. Chem.* **1980**, *45*, 3840–3846.

[13] Such a predominant formation of an (*E*)-configurated coupling product even from (*Z*)-1,2-dibromoethene has previously been observed. Cf.: ref.[7] and ref.[1] (Part 26).

[14] F. J. Weigert, R. L. Baird, J. R. Sharpley, *J. Am. Chem. Soc.* **1970**, *92*, 6630–6635.

[15] W. C. Still, M. Kahn, A. Mitra, *J. Org. Chem.* **1978**, *43*, 2923–2925.

[16] [16a] M. S. Baird, W. Nethercott, *Tetrahedron Lett.* **1983**, *24*, 605–608. – [16b] M. S. Baird, H. H. Hussain, W. Nethercott, *J. Chem. Soc., Perkin Trans. 1*, **1986**, 1845–1853.

[17] D. R. Coulson, *Inorg. Synth.* **1972**, *13*, 121–124.

[18] S. I. Miller, G. R. Ziegler, R. Wieleseck, *Org. Synth.* **1973**, collect. vol. 5, p. 921–923.

[19] R. Eastmond, D. R. M. Walton, *Tetrahedron* **1972**, 4591–4599.

[20] L. Brandsma in *Preparative Acetylenic Chemistry*, 2nd ed., Elsevier, Amsterdam, **1988**, p. 152–153.

[21] S. Untiedt, R. Walsh, A. de Meijere, unpublished results; S. Untiedt, Dissertation, Universität Hamburg, **1993**.

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