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Unprecedented McMurry Reactions with Acylsilanes: Enedisilane Formation versus Brook Rearrangement

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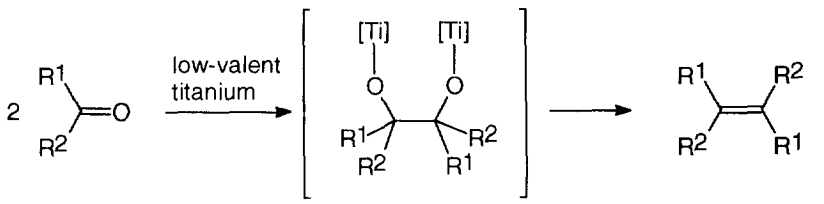
Abstract: The first inter- and intramolecular McMurry reactions of aroyltrimethylsilanes to substituted 1,2-bis(trimethylsilyl)ethene derivatives **2a-c** and **7** are described. A low-valent titanium reagent prepared by the reduction of $TiCl_3$ with Na on inorganic supports (Al_2O_3, NaCl, TiO_2) turned out to be best suited. Depending on the reaction conditions and on the particular substitution patterns of the substrates, Brook rearrangements of the intermediate 1,2-disilylated titanium-1,2-diolates leading to the formation of C,O-disilyl-enol ethers may compete with the McMurry deoxygenation pathway.

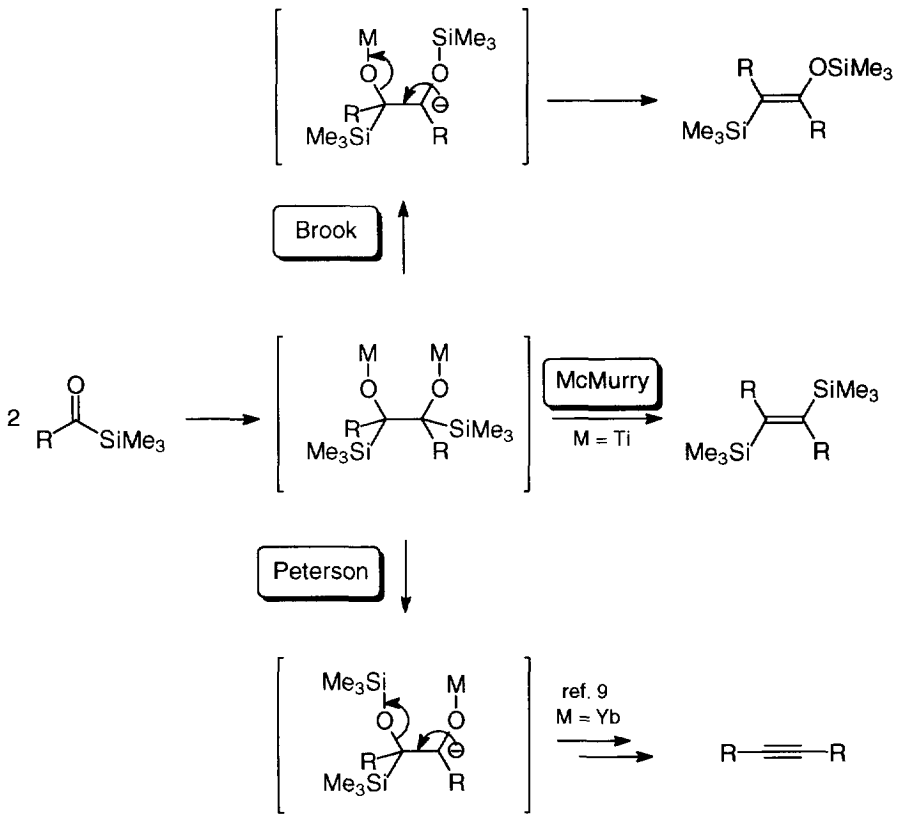
Organic chemistry with acylsilanes has expanded impressively in recent years stimulated by the greatly improved access to these valuable compounds.[1,2] In general, they behave like carbonyl groups of increased steric demand in reactions with nucleophiles, although they may serve as "umpoled" synthons after a selective cleavage of the C-Si bond.

While polar reactions of acylsilanes are reasonably well understood, conversions triggered by electron transfer remain largely unexplored.[3] For example, acylsilanes have not yet been used as substrates for McMurry reactions, despite their close relationship to carbonyl compounds.[4,5] McMurry reactions, the titanium-induced reductive coupling of aldehydes or ketones to alkenes, are generally discussed in terms of a single-electron transfer (s.e.t.) from the metal to the substrate. The ketyl radicals thus obtained dimerize to titanium-1,2-diolates, which are deoxygenated in the rate determining step to the respective alkene (Scheme 1).[4]



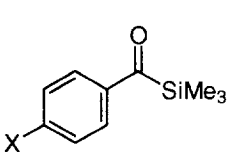
Scheme 1. Titanium-induced carbonyl coupling (McMurry reaction)

The scope of this reaction has recently been expanded beyond aldehydes and ketones as the traditional substrates. A new approach to aromatic heterocycles has been devised based upon the titanium-induced reduction of oxo-esters, oxo-amides, oxo-ureas etc.[6] These intramolecular cross-coupling reactions of functional groups with distinctly different redox potentials, however, are most probably initiated by a two-electron transfer rather than by s.e.t.[6a]

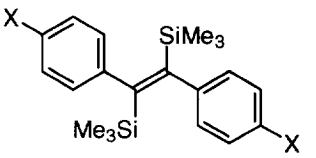


Scheme 2. Formation and reactions of 1,2-disilyl-1,2-diolates.

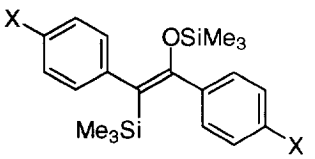
Acylsilanes may well react with low-valent titanium regardless of whether a single- or a two-electron transfer mechanism applies, since silicon is known to stabilize radicals as well as anions at the α-carbon atom. However, problems may arise *after* the initial C-C-bond formation. Thus, the deoxygenation of the pinacolate intermediates must compete with the known propensity of silyl groups to migrate to neighboring oxygen atoms. The latter results in either a Brook rearrangement[7] or a Peterson elimination[8] (Scheme 2). It was recently reported that 1,2-disilyl-1,2-diolates formed by an ytterbium-induced dimerization of acylsilanes exclusively afford alkynes via two Peterson reactions in cascade,[9] which shows that such silatropic rearrangements may in fact seriously rival other pathways.



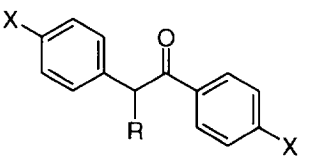
1 a X = H
b X = Br
c X = OMe



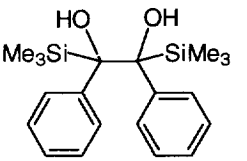
2a-c



3a-c



4 a X = R = H
b X = Br, R = H
c X = OMe, R = $SiMe_3$



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Gratifyingly however, when substrate **1a** was added to a refluxing suspension of low-valent titanium prepared by reduction of $TiCl_3$ with Na on Al_2O_3 ("high surface sodium") in DME,[10] a remarkably clean conversion took place with formation of (*E*)-1,2-bis(trimethylsilyl)-1,2-diphenylethene **2a** in 67% isolated yield (Table 1, entry 1). This product of a regular McMurry coupling of the acylsilane was obtained as a single isomer (vide infra). It was accompanied by 10% of the C,O-bis(trimethylsilyl)enol ether **3a**, which may stem from a competing Brook rearrangement of a common titanium-1,2-diolate intermediate. Although lowering the reaction temperature usually allows the McMurry reactions to be interrupted at the pinacol stage,[4] alkene **2a** was obtained with essentially the same yield when the reaction was carried out at 20 °C (*c.f.* entry 2). Diol **5** could only be isolated - albeit in low yield - when the reductive coupling was performed at -78 → 0°C with $[HTiCl{\cdot}(THF)_x]$ [11] as the active species (entry 6).

The preparative results turned out to be very sensitive to the reaction conditions. The activated titanium prepared by reduction of $TiCl_3$ with "high-surface sodium" on inorganic carriers gave by far the best results, with only minor differences in the yield of **2a** when NaCl or TiO_2 were chosen as support instead of Al_2O_3 (entries 1-5).[10] Other commonly used reagent combinations, however, such as $TiCl_3$/n C_8K (n = 2, 3)[12] or $TiCl_3/Zn$[6a,13] gave inferior results (entries 7, 8). Most strikingly, the use of commercial titanium powder activated by TMSCl[14] led to the selective formation of C,O-disilylenol ether **3a** (entry 9).[15]

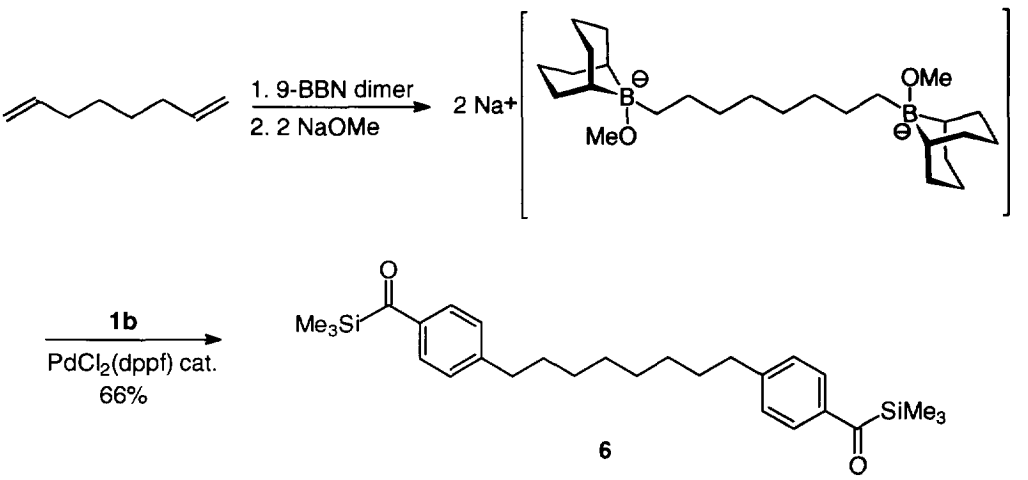
In order to test if the observed product distribution reflects the supposed competition between the McMurry- and the Brook reaction pathways, we treated the substituted acylsilanes **1b** and **1c** with low-valent titanium. It is well established that the rate of the C→O silyl group migration in C-silylated phenylcarbinols can be tuned by changing the electronic properties of the *para*-substituents X on the phenyl ring. The propensity for a Brook rearrangement follows the order X = -Br ≥ -Cl > -H ≈ -F > -t-Bu > -OMe.[7] In line with these kinetic data, substrate **1b** (X = Br) in fact affords ketone **4b** upon hydrolysis of the intermediate silylenol ether

3b as the major product (entry 10), whereas the more electron-rich derivative **1c** (X = OMe) follows the McMurry pathway with formation of 1,2-enedisilane **2c** in 56% yield together with only 6% of the corresponding ketone **4c** (entry 11).

Table 1. Titanium-induced reductive coupling reactions of aroyltrimethylsilanes.

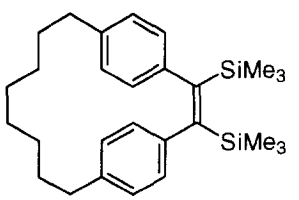
Entry	Substr.	Reagent	Solvent	T (°C)	t (h)	Product (Yield %)
1	**1a**	[Ti]/Al_2O_3	DME	84	1	**2a** (67%), **3a** (10%)
2	**1a**	[Ti]/Al_2O_3	DME	20	2.5	**2a** (66%)
3	**1a**	[Ti]/Al_2O_3	THF	65	5	**2a** (53%)[a]
4	**1a**	[Ti]/NaCl	THF	65	6	**2a** (63%), **4a** (21%)
5	**1a**	[Ti]/TiO_2	THF	65	2	**2a** (42%), **4a** (17%)
6	**1a**	HTiCl[b]	THF	-78→0	16	**2a** (12%), **5** (24%)
7	**1a**	$TiCl_3$/2 C_8K	THF	64	6	**2a** (39%), **4a** (54%)[c]
8	**1a**	$TiCl_3$/Zn	THF	65	4	**2a** (21%), **4a** (71%)[c]
9	**1a**	Ti/TMSCl[d]	DME	84	3.5	**3a** (61%)[e]
10	**1b**	[Ti]/NaCl	THF	65	1	**2b** (33%), **4b** (43%)
11	**1c**	[Ti]/Al_2O_3	THF	65	1	**2c** (56%), **4c** (6%)
12	**6**	[Ti]/Al_2O_3	DME	20	2.5	**7** (46%), **9a** (54%)
13	**6**	[Ti]/Al_2O_3	DME	84	2.5	**7** (49%), **8** (44%), **9a** (7%)

[a] Admixed with 1,2-bis-(trimethylsilyl)-1,2-diphenylethane (10 %), which was identified by the following characteristic spectroscopic data: ^{1}H NMR ($CDCl_3$, 200 MHz): δ 2.69 (s, 2H), -0.42 (s, 18H); ^{13}C NMR ($CDCl_3$, 50 MHz): δ 129.0 (d), 125.0 (d), 38.8 (d), -1.3 (q); MS: *m/z* (rel. intensity): 326 (20, M^+), 253 (35), 238 (18), 223 (14), 73 (100); ^{29}Si NMR ($CDCl_3$, 79.5 MHz): δ + 4.3 (J(Si-C) = 48 Hz). [b] Refers to [$HTiCl\cdot(THF)_x$], *c.f.* ref 11. [c] Some additional 1,2-diphenylethane-1,2-dione (7-8%) has been identified in the crude mixture by GC/MS. [d] Refers to commercial titanium powder activated by TMSCl. [e] GC-yield, *c.f.* experimental; isolated yield (HPLC): 52%.



Scheme 3. Synthesis of bis-aroylsilane **6** by two-fold Suzuki reaction.

Intramolecular couplings of bis-aroylsilanes are also possible. Thus, compound **6**, which was conveniently prepared from **1b** by a Suzuki-coupling approach (Scheme 3),[16] afforded the 18-membered 1,2-bis(trimethylsilyl)paracyclophan-1-ene **7** (McMurry pathway), together with C,O-disilylenol ether **8** or the hydrolyzed products **9a,b** thereof (Brook pathway) (entries 12,13). The good overall yields obtained in these macrocyclization reactions clearly show the bias of acylsilanes towards titanium-mediated C-C-bond formations, whereas the observed product distribution highlights once again the delicate balance in the affinity of the pinacolate oxygen atoms towards titanium versus silicon.



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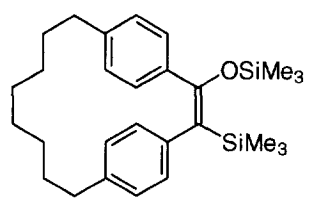

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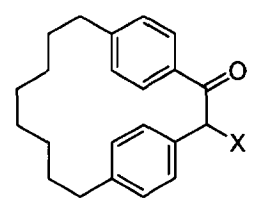
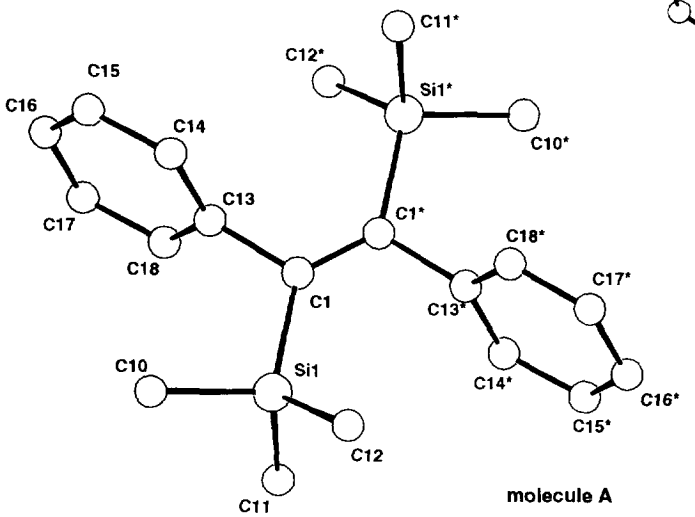


9 a X = $SiMe_3$
b X = H

In contrast to these smooth reactions of aroylsilanes, attempted couplings of *aliphatic* acyltrimethylsilanes were unsuccessful. Both acetyltrimethylsilane and phenylacetyltrimethylsilane reacted unselectively with low-valent titanium. Although the desired dimers could be detected by GC/MS, the crude mixtures were too complex to allow the isolation of substantial amounts of pure products. The reasons for this clearly different behavior of aroyl- and alkanoylsilanes are presently not clear.

Structural Investigations. Although the constitution of compound **2a** seems clear from its spectroscopic data, the melting point of our sample (114.5°C, DSC) did not exactly match that reported in the literature (116°C). Furthermore, the stereochemistry of this tetrasubstituted alkene had not been rigorously established.[17] Though an (*E*)-configuration seems more likely, a recent report has shown that contrary to previous assumptions the McMurry coupling of acetophenone preferentially affords the (*Z*)-alkene.[18] Since benzoylsilane **1a** is a silyl-analogue of acetophenone, we had to assign the stereochemistry of the coupling product **2a** unambiguously by X-ray analysis. The molecular structure is given in Figure 1 together with the numbering scheme. The asymmetric unit contains two independent half molecules with their centers of gravity on inversion centers. A static disorder about the central double bond fragment was established for one of the molecules (ratio 75:25), while the other molecule remains non-disordered. Disorder of the substituents at the sp^2-carbons, however, was not detected and therefore their intermolecular interactions may be considered as the driving forces for the packing of the molecules in the crystal. The central ethylene fragment is completely shielded by the substituents, and its relative orientation is thus less important for the molecular packing. This study confirmed the anticipated (*E*)-arrangement of the product.[19] The (*E*)-configuration was assigned to compounds **2b,c** by analogy.



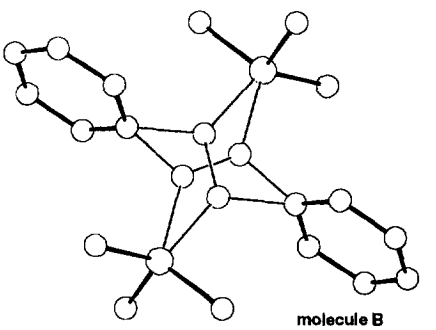


Fig. 1. Structure of compound **2a** in the crystal. Selected bond length [Å], bond angles [°] and torsion angles [°] of molecule A: C(1)-Si(1) 1.899(2), C(1)-C(1*) 1.325(3), C(1)-C(13) 1.522(3); Si(1*)-C(1*)-C(1) 128.0, C(1)-C(1*)-C(13*) 118.5; C(13)-C(1)-C(1*)-Si(1*) 0.7, C(1*)-C(1)-C(13)-C(18) 102.6, C(1)-C(1*)-C(13*)-C(14*) 81.1. The smaller figure shows the disordering of molecule B (ca. 75 : 25) in the crystal .

The NMR spectra of the hydrolytically rather labile α-TMS ketone **9a**, which was obtained as by-product in the reductive cyclization of the bis-acylsilane **6**, display an interesting structural feature. In the room temperature proton spectrum the signals from one of the aryl groups are very broad, indicating a restricted rotation of the ring. The ^1H and ^{13}C NMR spectra recorded in the range of 32°C to -60°C confirmed this

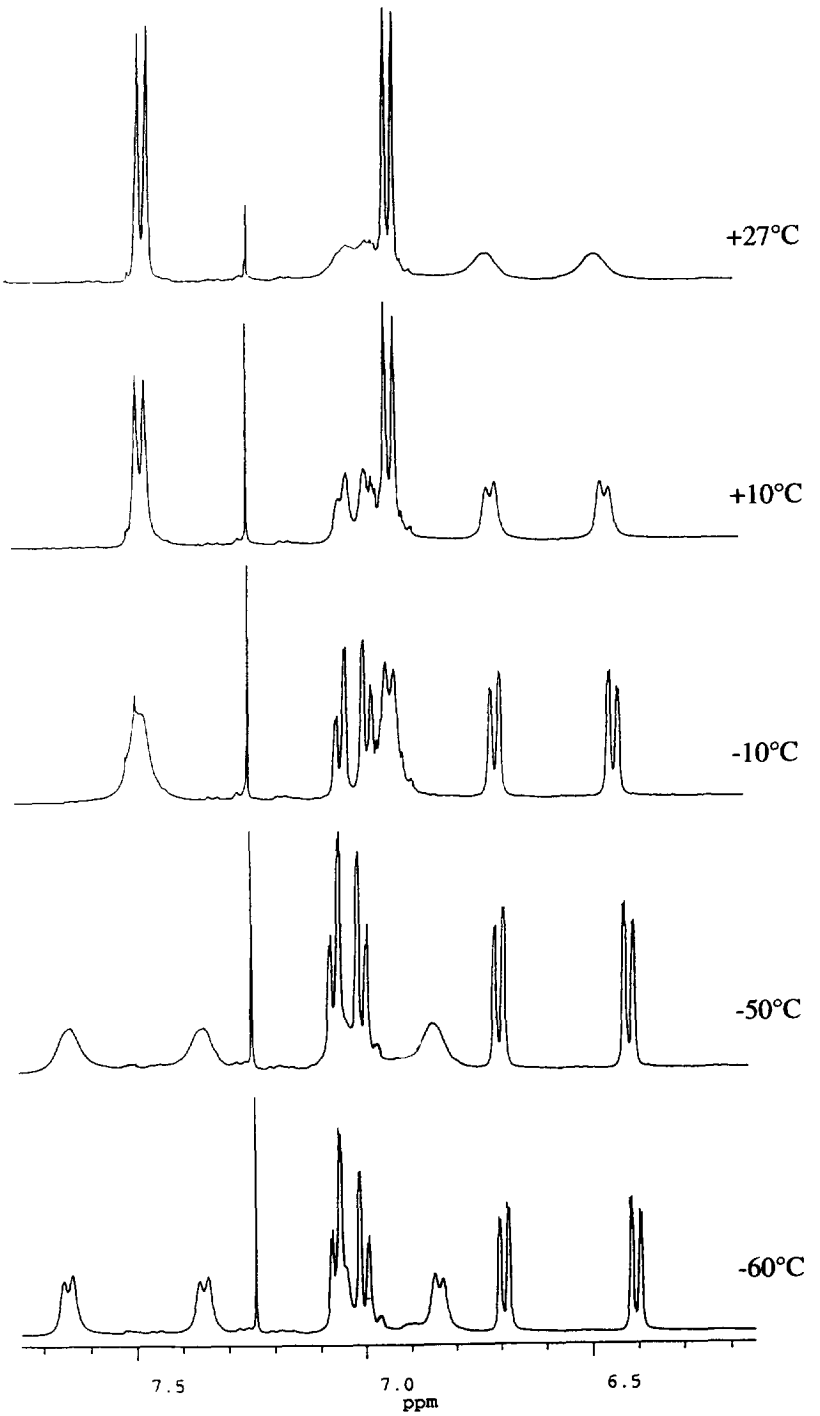


Fig. 2. The aromatic region of the 200 MHz ^{1}H NMR spectrum of compound **9a** at various temperatures shows that the restricted rotations of the two aryl rings have distinctly different rotation barriers. ^{13}C NMR spectra recorded at the same temperatures fully support this interpretation.

finding and show that at -60°C the other aryl ring also rotates slowly on the NMR time scale (Figure 2, Table 2). Using COSY and C,H correlated 2D spectra recorded at -60°C it was established that the ring with the greater barrier to rotation is bonded to the $CHSiMe_3$ group (ring B). While a full lineshape analysis was not carried out, the linewidths of the proton and ^{13}C signals of ring B at 32 °C allow the barriers to ring rotation to be estimated as ca. $\Delta G^{\neq}_{305} \sim 62$ kJ/mol and for ring A at -60 °C as $\Delta G^{\neq}_{213} \sim 46$ kJ/mol, respectively.

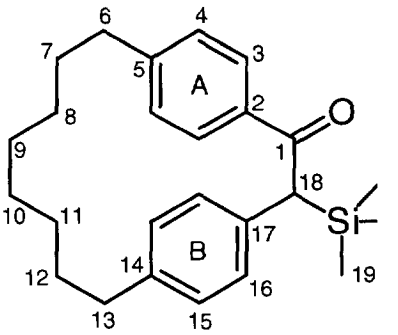


Table 2. The ^1H and ^{13}C NMR data of compound **9a**. All assignments, except were indicated by *, are unambiguous and were made using COSY and $^{13}C,^1H$-chemical shift correlated NMR spectra (the latter optimized for $^1J(C,H)$ and for $^nJ(C,H)$). Arbitrary numbering as shown.

position	δ_C (32 °C)	δ_C (-60°C)	^1J(CH) at 32°C	δ_H (32°C)	δ_H (-60°C)
1	203.1 (s)	203.2			
2	136.2 (s)	135.1			
3/3'	128.7 (d)	128.1/129.1	160±1	7.47 (d)	7.35 (d), 7.64 (d)
4/4'	128.3 (d)	128.1/128.5	158±1	6.92 (d)	6.84 (d), 7.05 (d)
5	146.0 (s)	146.3			
6	35.5 (t)	35.4	127±1	2.53	2.46 and 2.54
7	30.1 (t)	30.0	126±1	1.28 and 1.49	
8	25.3 (t)	25.0	123±2	0.53 and 0.70	
9	27.88* (t)	27.7	124±2	1.02 and 1.14	
10	27.93* (t)	27.7	124±2	1.02	
11	25.5 (t)	25.3	123±2	0.55	
12	31.0 (t)	30.9	127±2	1.28 and 1.40	
13	35.3 (t)	35.1	127±1	2.37 and 2.55	2.28 and 2.58
14	138.8 (s)	138.5			
15/15'	129.2 (d)	128.6/129.3	157±1	6.72 and 6.92	6.69 (d), 7.00 (d)
16/16'	127.8/129.8 (d)	127.2/129.5	broad	6.46 and 7.00	6.41 (d), 7.06 (d)
17	136.4 (s)	136.0			
18	50.0 (d)	48.7	115±1	3.95 (s)	4.02 (s)
19	-2.0 (q)	-2.4	120±1	0.15 (s)	0.11 (s)

EXPERIMENTAL

General. All reactions were carried out under Ar using Schlenk-techniques unless stated otherwise. For the instrumentation used see ref.[6a-c] Melting points were measured on a Gallenkamp apparatus (uncorrected) or by differential scanning calorimetry (DSC). The multiplicity in the ^{13}C NMR spectra refers to the geminal protons (DEPT). $TiCl_3$: Aldrich (99% purity). Titanium powder: Alfa, Johnson Matthey (99%, 325 mesh). TMSCl was purchased from Janssen and distilled prior to use. For the preparation of Na/Al_2O_3, Na/TiO_2 and Na/NaCl see ref.[10], for that of C_8K see ref.[12]. Other chemicals were purchased from Aldrich and used as received. The solvents were dried by distillation over the following drying agents: THF (Mg-anthracene), DME (Na/K-alloy). Flash chromatography: Merck silica gel 60 (230-400 mesh) using hexane/ethyl acetate in various proportions as eluent. Acylsilanes **1a-c** were prepared according to literature methods.[20] The COSY and C,H correlated spectra (optimized for ^1J(C,H) and for ^nJ(C,H), respectively) of compound **9a** were recorded on a Bruker AMX-300 at 32°C and -60°C using standard programs from the Bruker pulse library (COSY 90 and HXCO).

Crystal structure analysis of 2a.[19] Crystals were grown from hexane (20° → -78°C). $C_{20}H_{28}Si_2$, M_r = 324.6 $gmol^{-1}$, colorless crystals, crystal size 0.18 x 0.42 x 0.49 mm, a = 6.532(1), b = 8.941(1), c = 18.631(2) Å, V = 1007.7 $Å^3$, T = 293 K, d_{cal} = 1.07 g · cm^{-3}, μ = 1.67 cm^{-1}, Z = 2, triclinic, space group $P\bar{1}$ [No. 2], Enraf-Nonius CAD4 diffractometer, λ = 0.71069 Å, scan mode ω-2θ, 4755 measured reflections (+h, +k, +l) $[(\sin\theta)/\lambda]_{max}$ = 0.65 $Å^{-1}$, 4611 independent reflections, 3471 observed reflections [$I>2\sigma(I)$], structure solved by direct methods (SHELX86, Sheldrick, G. M. *Acta Cryst* **1990**, A46, 467-473), final refinement by least-squares (GFMLX, a modified version of ORFLS, Busing, W. R.; Martin, K. O.; Levy, H. A. Report ORNL-TM-305, Oak Ridge National Laboratory, Oak Ridge, TN, U.S.A. 1962), H atoms calculated and kept fixed in the final stage of refinement, R = 0.052, R_w = 0.061 for 198 refined parameters [$w = 1/\sigma^2(F_o)$], residual electron density 0.66 $eÅ^{-3}$.

1,8-Bis(4-trimethylsilylcarbonylphenyl)octane (6). To a suspension of 9-BBN dimer (3.99 g, 16.4 mmol) in THF (60 mL) was added dropwise a solution of 1,7-octadiene (1.81 g, 16.4 mmol) in THF (15 mL). After the slightly exothermic reaction had subsided, the solvent was evaporated to afford the respective bis(borane) as a colorless, viscous liquid (^{11}B NMR ($CDCl_3$): δ + 88.6). To a solution of this bis-borane (1.67 g, 4.7 mmol) in THF (120 mL) was added NaOMe (763 mg, 14.1 mmol) and the solution was stirred for 2 h to ensure quantitative formation of the corresponding bis-borate (^{11}B NMR (THF): δ -1.9). $PdCl_2$(dppf) (187 mg, 10 mol%) and acylsilane **1b** (2.1 g, 8.3 mmol) were added successively and the resulting mixture was refluxed for 1 h. After evaporation of the solvent, the residue was suspended in CH_2Cl_2 (100 mL), the precipitated NaBr was filtered off, the filtrate was evaporated and the remaining 9-MeO-9-BBN was removed *in vacuo* (10^{-3} Torr, 60°C). The crude product was purified by flash chromatography with hexane/ethyl acetate (20/1) as eluent, affording compound **6** as yellow syrup which slowly solidified (1.29 g, 66%). IR (cm^{-1}): 1720, 1700; ^1H NMR ($CDCl_3$, 200 MHz): δ 7.77 (d, J = 8.1 Hz, 4H), 7.27 (d, 4H), 2.65 (t, 4H), 1.63

(m, 4H), 1.33 (bs, 8H), 0.38 (s, 18H); ^{13}C NMR ($CDCl_3$, 50 MHz): δ 234.7 (s), 148.3 (s), 139.3 (s), 128.6 (d), 127.6 (d), 35.9 (t), 31.0 (t), 29.3 (t), 29.2 (t), -1.4 (q, J(Si-C) = 53 Hz); MS *m/z* (rel. intensity): 466 (100, M^+), 395 (11), 365 (18), 303 (8), 249 (8), 177 (13), 147 (41), 73 (48). $C_{28}H_{42}O_2Si_2$ (466.8): calc. C 72.04, H 9.06, Si 12.04; found C 71.54, H 8.92, Si 12.42.

General procedure for the reductive coupling of aroyltrimethylsilanes. To a stirred suspension of Na/Al_2O_3 (10 % w/w) (2.75 g, 9.8 mmol Na content)[10] in DME (50 mL) was added $TiCl_3$ (0.76 g, 4.9 mmol) and the resulting slurry was refluxed for 1 h. A solution of the acylsilane (1.6 mmol) in DME (5 mL) was then added and reflux continued until TLC showed complete conversion of the substrate (c.f. Table 1). The mixture was filtered through a pad of silica, the inorganic residues were thoroughly washed with THF in several portions, the combined filtrates were evaporated and the crude product purified by flash chromatography with mixtures of hexane/ethyl acetate in various proportions as eluent. The preparative results are summarized in Table 1, the analytical and spectroscopic data of the products obtained are compiled below.

(*E*)-1,2-Bis(trimethylsilyl)-1,2-diphenylethene (2a). mp 114.5 °C (DSC); ^1H NMR ($CDCl_3$, 200 MHz): δ 7.27 (t, J = 7, 4H), 7.18 (tt, J = 2, 7.5, 2H), 7.04 (dd, 4H), -0.36 (s, 18H); ^{13}C NMR ($CDCl_3$, 50 MHz): δ159.1 (s, J (Si-C) = 59.4 Hz), 145.8 (s), 128.1 (d), 127.6 (d), 125.6 (d), 0.24 (q, J (Si-C) = 51.7 Hz); MS *m/z* (rel. intensity): 324 (24, M^+), 309 (13), 251 (8), 221 (18), 135 (23), 73 (100); ^{29}Si NMR ($CDCl_3$, 79.5 MHz): δ - 8.2. $C_{20}H_{28}Si_2$ (324.6): calcd. C 74.00, H 8.70, Si 17.30; found C 73.87, H 8.50, Si 17.67.

1,2-Bis(4-bromophenyl)-1,2-bis(trimethylsilyl)ethene (2b). mp 176 °C (DSC); ^1H NMR ($CDCl_3$, 200 MHz): δ 7.43 (d, 4H), 6.91 (d, 4H), -0.33 (s, 18H); ^{13}C NMR ($CDCl_3$, 50 MHz): δ 159.0 (s, J(Si-C) = 58 Hz), 144.5 (s), 131.1 (d), 129.8 (d), 119.9 (d), 0.52 (q, J(Si-C) = 55 Hz); MS : *m/z* (rel. intensity): 480 (3, M^+), 401 (12), 313 (23), 213 (7), 73 (100); ^{29}Si NMR ($CDCl_3$, 79.5 MHz): δ -6.8. $C_{20}H_{26}Br_2Si_2$ (482.4): calcd. C 49.79, H 5.43, Br 33.13, Si 11.64; found C 49.89, H 5.42, Br 33.25, Si 11.54.

1,2-Bis(4-bromophenyl)ethanone (4b). mp 137 °C (DSC); IR (cm^{-1}): 1690; ^1H NMR ($CDCl_3$, 200 MHz): δ 7.84 (d, 2H), 7.59 (d, 2H), 7.44 (d, 2H), 7.11 (d, 2H), 4.19 (s, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 196.0 (s), 135.0 (s), 133.0 (s), 132.0 (d), 131.8 (d), 131.1 (d), 130.0 (d), 128.6 (s), 121.1 (s), 44.7 (t); MS: *m/z* (rel. intensity): 352 (3, M^+), 183 (100), 155 (16), 90 (10), 76 (12). $C_{14}H_{10}Br_2O$ (354.0): calcd. C 47.51, H 2.85, Br 45.14; found C 47.52, H 2.81, Br 44.92.

1,2-Bis(4-methoxyphenyl)-1,2-bis(trimethylsilyl)ethene (2c). mp 47-48 °C; ^1H NMR ($CDCl_3$, 200 MHz): δ 6.94 and 6.82 (AB, 8H), 3.81 (s, 6H), -0.35 (s, 18H); ^{13}C NMR ($CDCl_3$, 50 MHz): δ 159.3 (s, J(Si-C) = 61 Hz), 157.8 (s), 138.3 (s), 129.0 (d), 113.0 (d), 55.2 (q), 0.33 (q, J(Si-C) = 52 Hz); MS: *m/z* (rel. intensity): 384 (48, M^+), 369 (24), 311 (25), 296 (11), 281 (15), 204 (33), 165 (33), 73 (100); ^{29}Si NMR ($CDCl_3$, 79.5 MHz): δ -7.6. $C_{22}H_{32}O_2Si_2$ (384.6): calcd. C 68.69, H 8.40, Si 14.61; found C 68.64, H 8.41, Si 14.54.

1,2-Bis(4-methoxyphenyl)-2-trimethylsilylethanone (4c). IR (cm^{-1}): 1680, 1655; ^1H NMR ($CDCl_3$, 200 MHz): δ 7.92 (d, J = 8.9, 2H), 7.36 (d, 2H), 6.89 (d, 2H), 6.82 (d, 2H), 4.51 (s, 1H), 3.82 (s, 3H), 3.75 (s, 3H), -0.04 (s, 9H); ^{13}C NMR ($CDCl_3$, 50 MHz): δ 198.4 (s), 163.0 (s), 157.5 (s), 131.9 (d), 130.5 (d),

129.7 (s), 129.0 (d), 113.6 (d), 113.5 (d), 55.4 (q), 55.2 (q), 48.7 (d), -2.2 (q); MS *m/z* (rel. intensity): 328 (90, M^+), 313 (20), 285 (20), 135 (100), 73 (36); ^{29}Si NMR ($CDCl_3$, 79.5): δ +7.4.

Intramolecular coupling of compound 6. To a suspension of Na/Al_2O_3 (10 % w/w) (2.85 g, 10.2 mmol Na)[10] in DME (60 mL) was added $TiCl_3$ (790 mg, 5.1 mmol) and the resulting slurry was refluxed for 1 h to ensure complete reduction. A solution of compound **6** (397 mg, 0.85 mmol) in DME (25 mL) was added dropwise over a period of 2 h at that temperature and the heating was continued until TLC showed complete conversion of the substrate (2.5 h). Work-up as described above followed by flash-chromatography with hexane/ethyl acetate (20/1) as eluent afforded a white, crystalline product (339 mg) which turned out (GC) to be a mixture of compounds **7** (49%), **8** (44%) and **9** (7%). Analytically pure samples of these products were obtained by preparative HPLC (Shimadzu LC-8A with SIL-8A, Spark SPH-99; dynamax-5-C_{18} as stationary and acetonitrile as mobile phase; 308 K, 10 mL/min, 0.6 MPa; UV-detection). Compound **7**: 130 mg, mp 164 °C (DSC); ^{1}H NMR ($CDCl_3$, 200 MHz): δ 6.60 (d, 4H), 6.38 (d, 4H), 2.30 (t, 4H), 1.21 (m, 4H), 1.06 (m, 4H), 0.64 (m, 4H), 0.0 (s, 18H); ^{13}C NMR ($CDCl_3$, 50 MHz): δ 158.9 (s, J(Si-C) = 64 Hz); 144.0 (s), 137.7 (s), 127.5 (d), 127.4 (d), 35.5 (t), 30.2 (t), 26.8 (t), 24.6 (t), 1.6 (q, J(Si-C) = 52 Hz); MS: *m/z* (rel. intensity): 434 (100, M^+), 418 (18), 361 (41), 346 (33), 331 (66), 73 (78); ^{29}Si NMR ($CDCl_3$, 79.5 MHz): δ -8.1. $C_{28}H_{42}Si_2$ (434.8): calcd. C 77.35, H 9.73, Si 12.92; found C 76.97, H 9.85, Si 12.92. Compound **8**: 84 mg, ^{1}H NMR ($CDCl_3$, 200 MHz): δ 6.91 (d, 2H), 6.80 (d, 2H), 6.74 (d, 2H), 6.66 (d, 2H), 2.47 (m, 4H), 1.37 (m, 4H), 1.16 (m, 4H), 0.73 (m, 4H), 0.14 (s, 9H, -OTMS), 0.01 (s, 9H, -C-TMS); ^{13}C NMR ($CDCl_3$, 200 MHz): δ 159.7 (s), 141.0 (s), 139.8 (s), 137.9 (s), 136.6 (s), 129.9 (d), 129.5 (d), 127.7 (d), 127.5 (d), 121.6 (s), 35.2 (2 t), 30.4 (t), 29.9 (t), 27.3 (2 t), 25.1 (t), 24.9 (t), 1.0 (q), -0.05 (q); MS: *m/z* (rel. intensity): 450 (100, M^+), 435 (44), 147 (31), 73 (42); ^{29}Si NMR ($CDCl_3$, 79.5 MHz): δ +17.5 (O-TMS), -7.8 (C-TMS). Compound **9a**: mp 100-101 °C; for ^{1}H and ^{13}C NMR data see Table 2; MS: *m/z* (rel. intensity): 378 (100, M^+), 307 (11), 294 (15), 73 (19); ^{29}Si NMR ($CDCl_3$, 79.5 MHz): δ +1.1.

Reductive coupling of compound 1a with [HTiCl·$(THF)_x$]. To a suspension of [HTiCl·$(THF)_x$] (388 mg, 3.1 mmol)[11] in THF (5 mL) as added substrate **1a** (535 mg, 3.0 mmol) in THF (5 mL) at -78°C. The mixture was allowed to warm to room temperature and the course of the reaction was followed by a gas-burette. After the formation of H_2 had ceased the mixture was worked-up as described above. Flash chromatography of the crude product afforded enedisilane **2a** (60 mg, 12%), followed by 1,2-bis(trimethylsilyl)-1,2-dihydroxy-1,2-diphenylethane **5** (128 mg, 24%) with the following analytical data: IR (cm^{-1}): 3520; ^{1}H NMR ($CDCl_3$, 200 MHz): δ 7.24 (m, 10H), 2.74 (br s, -OH), -0.17 (s, 18H); ^{13}C NMR ($CDCl_3$, 50 MHz): δ 142.9 (s), 127.3 (d), 127.2 (d), 126.3 (d), 81.3 (s), -0.4 (q); MS: *m/z* (rel. intensity): 358 (<1, M^+), 340 (25), 252 (17), 178 (54), 147 (89), 135 (32), 75 (72), 73 (100).

Reductive coupling of 1a with commercial titanium powder/TMSCl: A suspension of titanium dust (563 mg, 11.8 mmol) and TMSCl (1.27 g, 11.7 mmol) in DME (8 mL) was refluxed for ≈ 70 h under Ar.[14] A solution of substrate **1a** (410 mg, 2.3 mmol) in DME (2 mL) was added and the slurry refluxed for 3.5 h until TLC showed complete conversion of the starting material. The mixture was filtered through a pad of silica, the inorganic residues were thoroughly washed with THF in several portions and the combined filtrates were evaporated. The residue (259 mg) was 88% pure in **3a** (i.e. 61%). An analytically pure sample of this product

was obtained by preparative HPLC (see above) as colorless crystals (192 mg, 52%): mp 50.5 (DSC); ^{1}H NMR ($CDCl_3$, 200 MHz): δ 7.11 (bs, 5H), 7.07 (m, 2H), 6.98 (m, 1H), 6.86 (m, 2H), 0.19 (s, 9H, -OTMS), 0.05 (s, 9H, C-TMS); ^{13}C NMR ($CDCl_3$, 50 MHz): δ 158.3 (s), 142.2 (s), 138.9 (s), 129.9 (2 d), 129.7 (2 d), 127.4 (2 d), 127.2 (3 d), 124.4 (d), 121.7 (s, J (Si-C) = 62.7 Hz), 0.94 (q, OTMS, J (Si-C) = 59.5 Hz), 0.09 (q, C-TMS, J (Si-C) = 53.5 Hz); MS *m/z* (rel. intensity): 340 (17, M^+), 178 (14), 147 (100), 73 (25); ^{29}Si NMR ($CDCl_3$, 79.5 MHz): δ +18.2 (OTMS), -6.8 (C-TMS). $C_{20}H_{28}OSi_2$ (340.6): calcd. C 70.52, H 8.28, Si 16.50; found C 70.32, H 8.55, Si 16.48.

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