Small Ring Systems

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Cross-Coupling Reaction of a Highly Strained Molecule: Synthesis of σ–π Conjugated Tetrahedranes**

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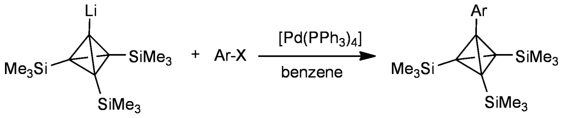
Tetrahedrane (C_4H_4), which consists of four cyclopropane rings, is one of the most severely strained cage compounds.[1] The high symmetry and unusual bonding of tetrahedrane have long fascinated synthetic and theoretical chemists.[1–3] The first stable tetrahedrane derivatives reported by Maier and co-workers were synthesized by photolysis of the corresponding cyclopentadienones,[4] (3-cyclopropenyl)diazomethanes,[5] or cyclobutadiene derivatives.[6] However, variation of the substituents was very limited and, in fact, required the presence of at least three *tert*-butyl groups. Since Maier's discovery of a synthetic method for stable tetrahedranes, only seven derivatives have been prepared by this method, because the starting materials are difficult to synthesize and the final photolytic step systematically has a low yield. Recently, the synthesis of a new tetrahedrane derivative, tetrakis(trimethylsilyl)tetrahedrane [$(Me_3Si)_4$THD], was reported by Maier et al. and ourselves.[7] This new tetrahedrane was synthesized by photoisomerization of the corresponding cyclobutadiene [$(Me_3Si)_4$CBD].[8] More recently, we reported an efficient isomerization of $(Me_3Si)_4$CBD into $(Me_3Si)_4$THD induced by $B(C_6F_5)_3$, which enabled a large-scale synthesis of $(Me_3Si)_4$THD.[9] Interestingly, the four σ-donating trimethylsilyl groups give this new tetrahedrane surprising thermal stability (up to 300 °C). However, this stability is not the most interesting feature of this new tetrahedrane. Rather, it is its ability to react with MeLi to form the tetrahedryllithium **1**.[10] The organolithium compound **1** has proven to be important in tetrahedrane chemistry because it gives access to a wide variety of heterosubstituted tetrahedrane derivatives from a single precursor, generally in reasonable to good yields.[10–13] However, the simple nucleophilic substitution of **1** with common electrophiles limits the type of substituent that may be introduced. New, efficient, and versatile synthetic routes are necessary to understand further the properties of tetrahedranes and highly strained σ-bond systems in general.

Transition-metal-catalyzed cross-coupling is one of the most straightforward and efficient methods for carbon–carbon bond formation.[14] The cross-coupling reaction can be performed on an incredible number of substrates using a wide variety of transition-metal catalysts which are often commercially available. Generally, one of the cross-coupling substrates has a carbon–metal bond where the new carbon–carbon bond is to be formed. This led us to consider the use of the tetrahedryllithium **1** (see Scheme 1) as a coupling partner in a cross-coupling reaction. In fact, several cross-coupling reactions have been reported between vinyl halides and organolithium reagents catalyzed by palladium. This led us to investigate the palladium-catalyzed cross-coupling reaction of the highly strained saturated hydrocarbon tetrahedryllithium with aryl halides. The results reported herein, show that this is a very powerful new synthetic procedure for synthesizing tetrahedrane derivatives which could not be synthesized by previous methods. The new aryl-substituted derivatives **2–7** (Scheme 1) have been characterized by NMR spectroscopy, and the tetrahedranes **5** and **7** have also been characterized by X-ray diffraction analysis. The electronic properties of these new tetrahedranes, which are the result of the σ–π conjugation mode between the strained tetrahedrane core and the aromatic ring, have also been investigated.



1 **2–7**

Scheme 1. Reaction of aryl halides with the tetrahedryllithium **1**.

Substituted tetrahedranes are also convenient alkyl coupling partners because, similar to *tert*-butyl groups,[15–17] they have no β-hydride atoms. Cross-coupling reactions with alkyl substrates are often complicated by β-hydride elimination.[18] This problem should be eliminated in the case of tetrahedranes. In general, the use of metals other than Li, such as Mg, Sn, B, or Zn, is preferred for coupling reactions for several reasons, including the high reactivity of organolithium reagents[19] and their tendency to take part in lithium–halide exchange reactions. However, Murahashi and co-workers have reported high yielding cross-coupling reactions of certain organolithium compounds with alkenyl halides using palladium and ruthenium catalysts.[20] These results, the lack of β-hydride atoms, and the relative reluctance of **1** to undergo lithium–halide exchange led us to investigate the cross-coupling reactions of **1** with aryl halides (Table 1). In addition, the magnesium- and stannyl-substituted tetrahedranes have been synthesized to compare their reactivity with that of **1**.

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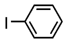
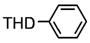
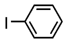
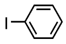
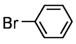
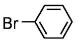
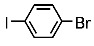
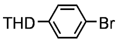
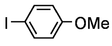
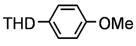
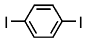
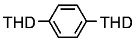
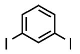
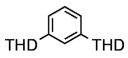
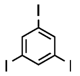
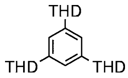
Table 1: Reaction of aryl halides with the tetrahedryllithium **1** to give the tetrahedrane derivatives **2**–**7**.

Entry	Ar–X	Product[a]		t	T [°C]	Yield [%][b]
1		THD– 	**2**	0.5 h	RT	93 (65)
2[c]			**2**	0.5 h	RT	46
3[d]			**2**	10 h	RT	0
4			**2**	10 days	RT	69 (59)
5			**2**	9 h	50	64 (53)
6			**3**	0.5 h	RT	84 (69)
7			**4**	0.5 h	RT	89 (69)
8			**5**	0.5 h	RT	(58)
9			**6**	0.5 h	RT	(65)
10			**7**	1 h	100	(50)

[a] THD = tris(trimethylsilyl)tetrahedryl group. [b] Yields were calculated based on ^{1}H NMR signals. Yields of isolated products are given within parentheses. [c] THF was used as the solvent instead of benzene. [d] Without palladium catalyst.

The magnesium- and stannyl-substituted tetrahedranes, new metal-substituted tetrahedrane derivatives, were prepared by the transmetallation reaction of **1** with magnesium chloride and tributyltin chloride, respectively. With these three coupling partners available, we set out to test the cross-coupling reaction with iodobenzene using the commercially available palladium catalyst [Pd(PPh$_3$)$_4$]. The reaction of metallotetrahedranes and iodobenzene was carried out at room temperature using 15 mol% of the catalyst. In the case of **1** the reaction proceeded cleanly and quickly to give the phenyl tetrahedrane **2** in 93% yield (Table 1, entry 1). The reaction of both the magnesium- and stannyl-substituted tetrahedrane with iodobenzene was conducted under identical reaction conditions, but no coupling reaction occurred (see Table S1 in the Supporting Information). Low yields of the desired product were obtained by heating the magnesium tetrahedrane while no product could be detected even upon extended heating of the stannyl tetrahedrane.

Clearly, the lithium tetrahedrane gives the best results, so we sought to further optimize the reaction conditions and test a variety of aryl coupling partners. The choice of solvent proved to be important in obtaining the optimal yield. The reaction in benzene proceeded cleanly and afforded the desired product in high yield, whereas in THF the yield of the desired product was significantly lower (Table 1, entry 2). Presumably, the polar solvent facilitates the lithium–halogen exchange reaction, whereas hydrocarbon solvents prevent this side reaction almost completely. The palladium catalyst is essential to the reaction and no reaction was observed without the palladium catalyst even upon extended reaction times (entry 3).

Next, phenyl bromide was employed as a substrate. The reaction proceeded slowly at room temperature but produced the desired product in moderate yield after ten days (Table 1, entry 4). This result is not unexpected as it is well known that aryl bromides are significantly less reactive than aryl iodides. With this in mind, the same reaction was conducted at 50 °C, at which a marked enhancement of the reaction rate was observed. The desired product was obtained in nearly the same yield after 9 hours as after ten days at room temperature (entry 5). The difference in reaction rates between aryl iodides and bromides is significant enough that when *p*-bromoiodobenzene was used as the substrate, the coupling reaction proceeded selectively at the iodo-substituted position, again in good yield (entry 6). An electron-rich aryl iodide, *p*-iodoanisole, also rapidly reacted to give an electron donating group substituted aryl tetrahedrane (entry 7). Remarkably, di- and tritetrahedrylbenzene derivatives could also be synthesized by the same method in good yields (entries 8–10). It is noteworthy that all of these reactions proceeded cleanly in good yields in spite of using a common palladium(0) catalyst.

The tetrahedrane derivatives **2**–**7** were stable in air and at elevated temperature (melting point of **7**: 197–200 °C). The most important stabilizing factor should be attributed to the electronic effect of the trimethylsilyl groups, as found in (Me$_3$Si)$_4$THD.[7] The ^{1}H, ^{29}Si, and ^{13}C NMR spectra of **7** in [D$_6$]benzene demonstrated its high symmetry. Only two signals were observed for the trimethylsilyl groups (δ = 0.25 ppm) and aromatic protons (δ = 7.20 ppm) in the ^{1}H NMR spectra, and one signal for the ^{29}Si NMR (δ = −2.2 ppm) spectra, and five signals appeared at δ = −15.0 (ring C-Si), 0.2 (SiMe$_3$), and 5.2 (*C*-C$_6$H$_5$), 126.9 and 133.6 ppm (aromatic C) in the ^{13}C NMR spectrum. The large upfield shift of the ring C atom is typical for tetrahedranes.[7,10–13]

The molecular structures of **5** and **7** were determined by X-ray crystallography (Figures 1 and 2).[21] The C–C bond

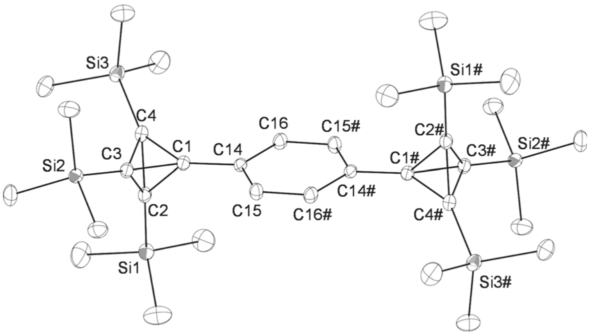


Figure 1. The structure of **5** (ORTEP; thermal ellipsoids shown at at 30% probability; hydrogen atoms omitted for clarity). Selected bond lengths [Å] and angles [°]: C1–C14 1.4586(16), C1–C2 1.5074(17), C1–C3 1.4733(17), C1–C4 1.4698(17), C2–C3 1.5051(18), C2–C4 1.5058(18), C3–C4 1.5403(18), C14–C15 1.3893(18), C14–C16 1.3924(18), C15–C16# 1.3866(18), Si1–C2 1.8217(13), Si2–C3 1.8288(13), Si3–C4 1.8264(14); C2-C1-C3 60.64(8), C3-C1-C4 63.12(9), C4-C1-C2 60.75(9), C1-C2-C3 58.56(8), C1-C2-C4 58.39(8), C1-C3-C4 58.33(8), C1-C3-C2 60.80(8), C1-C4-C2 60.86(8), C1-C4-C3 58.56(8), C2-C3-C4 59.26(8), C3-C4-C2 59.21(8), C4-C2-C3 61.54(9).

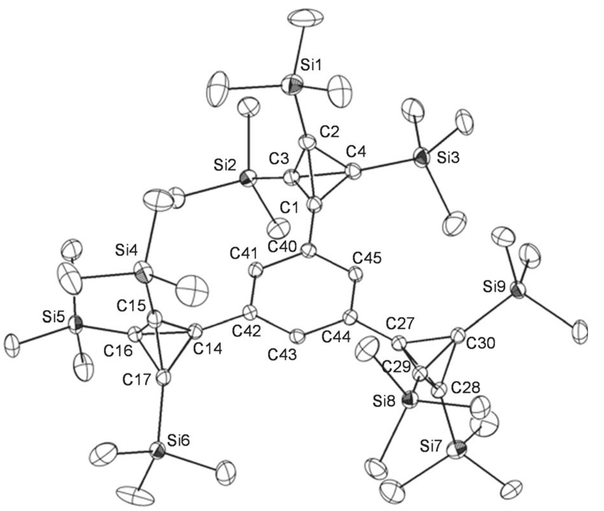
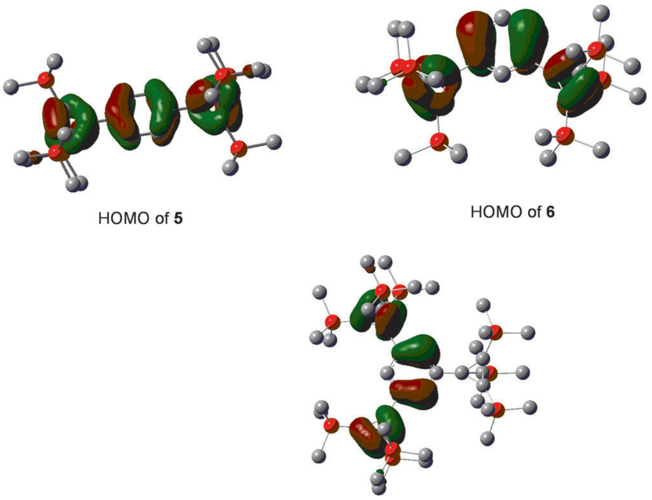


Figure 2. The structure of **7** (ORTEP; thermal ellipsoids shown at 30% probability; hydrogen atoms omitted for clarity). Selected bond lengths [Å]: C1–C40 1.456(2), C1–C4 1.469(2), C1–C3 1.480(2), C1–C2 1.505(2), C2–C3 1.498(3), C2–C4 1.514(3), C3–C4 1.539(2), C14–C42 1.458(2), C14–C16 1.472(2), C14–C17 1.477(2), C14–C15 1.499(2), C15–C17 1.503(3), C15–C16 1.509(3), C16–C17 1.532(2), C27–C44 1.455(2), C27–C29 1.476(2), C27–C30 1.476(2), C27–C28 1.500(2), C28–C30 1.507(2), C28–C29 1.507(2), C29–C30 1.532(2), C40–C45 1.394(2), C40–41 1.397(2), C41–C42 1.393(2), C42–C43 1.395(2), C43–C44 1.393(2), C44–C45 1.396(2).


HOMO of **5**

HOMO of **6**

HOMO of **7**

Figure 3. HOMOs of **5**, **6**, and **7**.

lengths between the tetrahedrane skeleton and aryl substituent are 1.4586(16) Å in **5** and 1.456(2) Å (av) in **7**, which are significantly shorter than a typical C(sp^3)−C(sp^2) single bond (1.507 Å).[22] This shortening is the result of the high s character of the orbitals involved in this bond as well as the σ–π conjugation between the tetrahedryl moiety and aromatic ring.[23–25] The C−C bond lengths of the skeleton of the tetrahedrane are also influenced by the substituents. When the electronegativity increases (C: 2.55 versus Si: 1.90, Pauling scale),[26] the s character of the exocyclic bond decreases, which causes the shortening of the C(Ar)−C(SiMe$_3$) bond compared to the C(SiMe$_3$)−C(SiMe$_3$) bond length. Thus, the C(Ar)−C(SiMe$_3$) bond lengths are 1.4835(17) Å (av) in **5** and 1.483(2) Å (av) in **7**, whereas the C(SiMe$_3$)−C(SiMe$_3$) bond lengths are 1.5171(18) Å (av) in **5** and 1.508(2) Å (av) in **7**.

In the UV/Vis spectra of **5**, **6**, and **7**, the absorption maxima were observed at $\lambda = 285$ nm ($\varepsilon = 2.0\times10^4$ cm^{-1}M^{-1}) for **5**, $\lambda = 262$ nm ($\varepsilon = 2.4\times10^4$ cm^{-1}M^{-1}) for **6**, and $\lambda = 265$ nm ($\varepsilon = 3.8\times10^4$ cm^{-1}M^{-1}) for **7**. To understand the electronic spectra, DFT calculations on the compounds **5**, **6**, and **7** were performed at the B3LYP level using the 6-31G(d) basis set with the GAUSSIAN-03 program. The molecular orbitals of **5**–**7** show that the HOMO consists of the mixing of the tetrahedrane σ core and aryl π system (as depicted in Figure 3), whereas the LUMO consists of the π* orbital of the aromatic ring: **5**: HOMO (−5.06 eV); **6**: HOMO (−5.22 eV); **7**: (HOMO (−5.22 eV). These computational results are consistent with both the spectroscopic and structural properties, thus suggesting the electronic spectra are affected by the different substitution pattern on the aromatic ring. The considerable bathochromic shift of **5** with *para* substitution compared with **6** and **7** clearly indicates the existence of extended σ–π conjugation between the tetrahedrane σ core and the aryl π system. The difference of the *meta* versus *para* substitution is rationalized by the linear combination of atomic orbitals, as can be seen in the HOMOs of **5** and **6**, as illustrated in Figure 3. The decrease in the degree of delocalization by *meta*-phenylene bridging compared to that of a *para* connection has been well established experimentally and theoretically.[27]

In summary, we have presented here a new efficient method for the preparation of functionalized tetrahedranes by palladium-catalyzed cross-coupling reaction of tetrahedryllithium with aryl halides. This new synthetic route affords a variety of new aryl-substituted tetrahedrane derivatives under ambient reaction conditions in good to excellent yields. Moreover, the electronic spectra of the aryl-substituted tetrahedranes **5**, **6**, and **7**, having different substitution patterns, clearly show the other properties of tetrahedranes caused by the difference in interaction mode between the highly strained tetrahedrane core and the aryl π system.

Experimental Section

Tetrakis(trimethylsilyl)tetrahedrane[7] (50 mg, 0.15 mmol) and methyllithium (4 mg, 0.19 mmol) were placed in a reaction tube and dry, oxygen-free tetrahydrofuran was introduced by vacuum transfer. After 2 days, all of the tetrakis(trimethylsilyl)tetrahedrane was consumed to produce a quantitative formation of the tetrahedryllithium **1**.[10] After removal of THF in vacuo, aryl halide (0.18 mmol, 1.2 equiv), tetrakis(triphenylphosphine)palladium (25 mg, 0.022 mmol, 15 mol%), and benzene (2 mL) were added, and the reaction mixture was stirred under the appropriate reaction conditions (see Table 1). After removal of the solvent, the reaction mixture was separated by HPLC [MeOH/*t*BuOMe (1:1)] to afford the cross-coupling product.

5: 58% (white crystals, 26 mg); mp = 178–182 °C; ^{1}H NMR (400 MHz, [D$_6$]benzene) $\delta = 0.18$ (s, 54 H), 7.38 ppm (s, 4 H); ^{13}C{H} NMR (100.6 MHz, [D$_6$]benzene) $\delta = -14.9$, 0.0, 5.1, 129.4, 131.1 ppm; ^{29}Si NMR (79.5 MHz, [D$_6$]benzene) $\delta = -2.3$ ppm;

HRMS (APCI) calcd for $C_{32}H_{58}Si_6H$ 611.3227; found: 611.3230 $[M+H]^+$; UV/Vis (hexane): λmax (ε): 285 nm (2.0×10^4 $cm^{-1}M^{-1}$).

6: 65% (white crystals, 29 mg); mp = 140–142 °C; ^{1}H NMR (400 MHz, [D$_1$]chloroform) $\delta = 0.14$ (s, 54 H), 6.94 (d, $J = 8.0$ Hz, 2 H), 7.02 (s, 1 H), 7.13 ppm (t, $J = 8.0$ Hz, 1 H); ^{13}C (100.6 MHz, [D$_1$]chloroform) $\delta = -15.2$, 0.0, 4.7, 126.0, 127.9, 128.9, 133.5 ppm; ^{29}Si (79.5 MHz, [D$_1$]chloroform) $\delta = -2.2$ ppm; HRMS (APCI) calcd for $C_{32}H_{58}Si_6H$ 611.3232; found: 611.3262 $[M+H]^+$; UV/Vis (hexane): λmax (ε): 262 nm (2.4×10^4 $cm^{-1}M^{-1}$).

7: 50% (white crystals, 20 mg); mp = 197–200 °C; ^{1}H NMR (400 MHz, [D$_6$]benzene) $\delta = 0.25$ (s, 81 H), 7.20 ppm (s, 3 H); ^{13}C{H} NMR (100.6 MHz, [D$_6$]benzene) $\delta = -15.0$, 0.2, 5.2, 126.9, 133.6 ppm; ^{29}Si NMR (79.5 MHz, [D$_6$]benzene) −2.2; HRMS (APCI) calcd for $C_{45}H_{84}Si_9H$ 877.4569; found: 877.4559 $[M+H]^+$; UV/Vis (hexane): λmax (ε): 265 nm (3.8×10^4 $cm^{-1}M^{-1}$).

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[1] For reviews on tetrahedranes, see: a) G. Maier, *Angew. Chem.* **1988**, *100*, 317; *Angew. Chem. Int. Ed. Engl.* **1988**, *27*, 309; b) G. Maier, *Pure Appl. Chem.* **1991**, *63*, 275; c) A. de Meijere, S. I. Kozhushkov, H. Schill, *Chem. Rev.* **2006**, *106*, 4926; d) V. Ya. Lee, A. Sekiguch, in *Strained Hydrocarbons* (Ed.: H. Dodziuk), Wiley-VCH, Weinheim, **2009**; chap. 2.

[2] For theoretical studies, see: a) M. Balci, M. L. McKee, P. von R. Schleyer, *J. Phys. Chem. A* **2000**, *104*, 1246; b) A. Nemirowski, H. P. Reisenauer, P. R. Schreiner, *Chem. Eur. J.* **2006**, *12*, 7411.

[3] a) R. F. Peterson Jr. , R. T. K. Baker, R. L. Wolfgang, *Tetrahedron Lett.* **1969**, *10*, 4749; b) P. B. Shevlin, A. P. Wolf, *J. Am. Chem. Soc.* **1970**, *92*, 406; c) L. B. Rodewald, H. Lee, *J. Am. Chem. Soc.* **1973**, *95*, 623; d) G. Maier, M. Hoppe, K. Lanz, H. P. Reisenauer, *Tetrahedron Lett.* **1984**, *25*, 5645.

[4] a) G. Maier, S. Pfriem, U. Schäfer, R. Matusch, *Angew. Chem.* **1978**, *90*, 552; *Angew. Chem. Int. Ed. Engl.* **1978**, *17*, 520; b) G. Maier, S. Pfriem, U. Schäfer, K.-D. Malsch, R. Matusch, *Chem. Ber.* **1981**, *114*, 3965.

[5] a) G. Maier, F. Fleischer, *Tetrahedron Lett.* **1991**, *32*, 57; b) G. Maier, F. Fleischer, *Liebigs Ann.* **1995**, 169; c) G. Maier, F. Fleischer, H.-O. Kalinowski, *Liebigs Ann.* **1995**, 173.

[6] a) G. Maier, D. Born, *Angew. Chem.* **1989**, *101*, 1085; *Angew. Chem. Int. Ed. Engl.* **1989**, *28*, 1050; b) G. Maier, R. Wolf, H.-O. Kalinowski, *Angew. Chem.* **1992**, *104*, 764; *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 738; c) G. Maier, R. Wolf, H.-O. Kalinowski, R. Boese, *Chem. Ber.* **1994**, *127*, 191; d) G. Maier, R. Wolf, H.-O. Kalinowski, *Chem. Ber.* **1994**, *127*, 201.

[7] G. Maier, J. Neudert, O. Wolf, D. Pappusch, A. Sekiguchi, M. Tanaka, T. Matsuo, *J. Am. Chem. Soc.* **2002**, *124*, 13819.

[8] a) G. Maier, J. Neudert, O. Wolf, *Angew. Chem.* **2001**, *113*, 1719; *Angew. Chem. Int. Ed.* **2001**, *40*, 1674; b) A. Sekiguchi, M. Tanaka, T. Matsuo, H. Watanabe, *Angew. Chem.* **2001**, *113*, 1721; *Angew. Chem. Int. Ed.* **2001**, *40*, 1675.

[9] M. Nakamoto, Y. Inagaki, T. Ochiai, M. Tanaka, A. Sekiguchi, *Heteroat. Chem.* **2011**, *22*, 412.

[10] A. Sekiguchi, M. Tanaka, *J. Am. Chem. Soc.* **2003**, *125*, 12684.

[11] M. Tanaka, A. Sekiguchi, *Angew. Chem.* **2005**, *117*, 5971; *Angew. Chem. Int. Ed.* **2005**, *44*, 5821.

[12] M. Nakamoto, Y. Inagaki, M. Nishina, A. Sekiguchi, *J. Am. Chem. Soc.* **2009**, *131*, 3172.

[13] T. Ochiai, M. Nakamoto, Y. Inagaki, A. Sekiguchi, *J. Am. Chem. Soc.* **2011**, *133*, 11504.

[14] a) *Metal-Catalyzed Cross-Coupling Reactions* (Eds.: F. Diederich, P. J. Stang), Wiley-VCH, Weinhein, **1998**; b) *Metal-Catalyzed Cross-Coupling Reactions, 2nd Completely Revised and Enlarged ed.*, *Vol. 1* (Eds.: A. de Meijere, F. Diederich), Wiley-VCH, Weinheim, **2004**; c) *Metal-Catalyzed Cross-Coupling Reactions, 2nd Completely Revised and Enlarged ed.*, *Vol. 2* (Eds.: A. de Meijere, F. Diederich), Wiley-VCH, Weinheim, **2004**.

[15] For examples of cross-coupling reactions between tertiary alkyl nucleophiles and sp^2 centers of aryl, heteroaryl, or vinyl electrophiles, see: a) S. M. Neumann, J. K. Kochi, *J. Org. Chem.* **1975**, *40*, 599; b) R. S. Smith, J. K. Kochi, *J. Org. Chem.* **1976**, *41*, 502; c) T. Hayashi, M. Konishi, K. Yokota, M. Kumada, *Chem. Lett.* **1980**, 767; d) H. Künzer, S. Berger, *J. Org. Chem.* **1985**, *50*, 3222; e) D. H. Burns, J. D. Miller, H. K. Chan, M. O. Delaney, *J. Am. Chem. Soc.* **1997**, *119*, 2125; f) G. Cahiez, H. Avedissian, *Synthesis* **1998**, 1199; g) L. K. Ottesen, F. Ek, R. Olsson, *Org. Lett.* **2006**, *8*, 1771; h) L. Hintermann, L. Xiao, A. Labonne, *Angew. Chem.* **2008**, *120*, 8370; *Angew. Chem. Int. Ed.* **2008**, *47*, 8246; i) J.-B. Langlois, A. Alexakis, *Chem. Commun.* **2009**, 3868; j) C. Lohre, T. Dröge, C. Y. Wang, F. Glorius, *Chem. Eur. J.* **2011**, *17*, 6052; k) A. Joshi-Pangu, C. Y. Wang, M. R. Biscoe, *J. Am. Chem. Soc.* **2011**, *133*, 8478.

[16] For examples of cross-coupling reactions between tertiary alkyl nucleophiles and C(sp^3) electrophiles, see: a) J. G. Donkervoort, J. L. Vicario, J. Jastrzebski, R. A. Gossage, G. Cahiez, G. van Koten, *J. Organomet. Chem.* **1998**, *558*, 61; b) G. Cahiez, C. Chaboche, M. Jézéquel, *Tetrahedron* **2000**, *56*, 2733; c) J. Terao, A. Ikumi, H. Kuniyasu, N. Kambe, *J. Am. Chem. Soc.* **2003**, *125*, 5646; d) J. Terao, H. Todo, S. A. Begum, H. Kuniyasu, N. Kambe, *Angew. Chem.* **2007**, *119*, 2132; *Angew. Chem. Int. Ed.* **2007**, *46*, 2086; e) P. Ren, L. A. Stern, X. Hu, *Angew. Chem.* **2012**, *124*, 9244; *Angew. Chem. Int. Ed.* **2012**, *51*, 9110.

[17] Catalytic cross-coupling reactions of cage compounds without β-hydride elimination have been reported. See: a) J. D. Rehm, B. Ziemer, G. Szeimies, *Eur. J. Org. Chem.* **1999**, 2079; b) A. S. K. Hashmi, A. Vollmer, G. Szeimies, *Liebigs Ann.* **1995**, 471; c) G. Kottirsch, G. Szeimies, *Chem. Ber.* **1990**, *123*, 1495; d) G. Kottirsch, K. Polborn, G. Szeimies, *J. Am. Chem. Soc.* **1988**, *110*, 5588.

[18] R. Jana, T. P. Pathak, M. S. Sigman, *Chem. Rev.* **2011**, *111*, 1417.

[19] E. Negishi, K. Akiyoshi, T. Takahashi, *J. Chem. Soc. Chem. Commun.* **1987**, 477.

[20] a) S. Murahashi, M. Yamamura, K. Yanagisawa, N. Mita, K. Kondo, *J. Org. Chem.* **1979**, *44*, 2408; b) S. Murahashi, *J. Organomet. Chem.* **2002**, *653*, 27.

[21] Crystal structure analysis of **5** and **7**: single crystals were grown from a toluene solution. Diffraction data were collected at 120 K on a Mac Science DIP2030 Image Plate Diffractometer with a rotating anode (50 kV, 90 mA) employing graphite-monochromatized Mo$_{K\alpha}$ radiation ($\lambda = 0.71070$ Å). Crystal data for **5** at 120 K: $C_{32}H_{58}Si_6$, $M_r = 611.32$, monoclinic, space group $C2/c$, $a = 15.4164(8)$ Å, $b = 10.1224(5)$ Å, $c = 27.0387(14)$ Å, $\beta = 102.573(1)°$, $V = 4118.2(4)$ Å^3, $Z = 4$, $\rho_{calcd} = 0.986$ g cm^{-3}. The final R factor was 0.0343 ($R_w = 0.0845$ for all data) for 4668 reflections with $I > 2\sigma(I)$, GOF = 1.062. Crystal data for **7**·0.25 C_7H_8 at 120 K: $C_{46.75}H_{86}Si_9$, MW = 900.97, monoclinic, space group $C2/c$, $a = 62.891(4)$ Å, $b = 15.5046(9)$ Å, $c = 25.5906(15)$ Å, $\beta = 97.4010(10)°$, $V = 24745(2)$ Å^3, $Z = 16$, $\rho_{calcd} = 0.967$ g cm^{-3}. The final R factor was 0.0432 ($R_w = 0.1262$ for all data) for 26338 reflections with $I > 2\sigma(I)$, GOF = 1.045. The structure was solved by the direct method, using the SIR-92 program, and refined by the full-matrix least-squares method using SHELXL-97. CCDC 941572 and 941573 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

[22] F. H. Allen, O. Kennard, D. G. Watson, L. Brammer, A. G. Orpen, R. Taylor, *J. Chem. Soc. Perkin Trans. 2* **1987**, S1.

[23] The s character of the C_{ring}–H bond in the hydrogen-substituted tetrahedrane H–$C_4(SiMe_3)_3$ was estimated to be 48 % by the very large C–H coupling constant ($^1J_{C\text{-}H} = 255.6$ Hz; Ref. [10]).

[24] Single bonds between sp^2 or sp carbon atoms (e.g., the central C–C bonds in 1,3-butadiene and 1,3-butadiyne) are certainly short: the phenomenon can be usually explained in terms of hybridization.

[25] For discussion of σ–π conjugation between the tetrahedryl moiety and aromatic ring in C_6F_5-$C_4(SiMe_3)_3$ by UV/photoelectron spectroscopy, see: A. Chrostowska, A. Dargelos, P. Baylère, A. Graciaa, Y. Inagaki, M. Nakamoto, V. Ya. Lee, A. Sekiguchi, *ChemPlusChem* **2013**, *78*, 398.

[26] J. Emsley, *The Elements*, *3rd ed.*, Oxford University Press, Oxford, **1998**.

[27] L. Pascal, J. J. Vanden Eynde, Y. Van Haverbeke, P. Dubois, A. Michel, U. Rant, E. Zojer, G. Leising, L. O. Van Dorn, N. E. Gruhn, J. Cornil, J. L. Brédas, *J. Phys. Chem. B* **2002**, *106*, 6442.