On the regioselectivity of alkylation of the (trimethylsilyl)tetramethylcyclopentadienide anion. A new approach to the synthesis of 1,2,3,4-tetramethylfulvene

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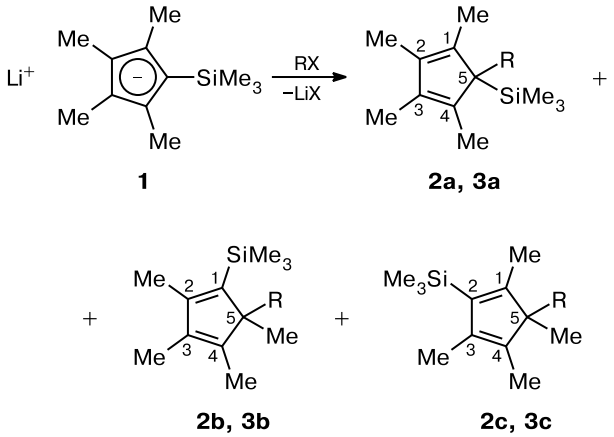
The regioselectivity of alkylation of lithium (trimethylsilyl)tetramethylcyclopentadienide $C_5Me_4SiMe_3^-Li^+$ was studied by ^1H and ^{13}C NMR spectroscopy using its reactions with MeI, MeOTs, $ClCH_2CH_2Br$, and $ClCH_2CH_2I$ in different solvents as representative examples. Sterically non-hindered MeI and MeOTs presumably attack the C atom bonded to the silyl group giving 1,2,3,4,5-pentamethylcyclopentadienylsilane. For bulkier alkyl halides, such as $ClCH_2CH_2Br$ and $ClCH_2CH_2I$, the regioselectivity of alkylation changes to form preferentially *gem*-dialkyl-substituted cyclopentadienes. The reaction of $C_5Me_4SiMe_3^-Li^+$ with formaldehyde affords 1,2,3,4-tetramethylfulvene in a high yield, providing an alternative synthetic approach to a number of ω-functionalized peralkylated cyclopentadienes. The quantum-chemical calculations of the $C_5Me_4SiMe_3^-$ anion by the RHF and DFT (RMPW1PW91) methods in the valence-split 6-311+G(d,p) basis set are in good agreement with the experimental data.

Key words: trimethylsilyl-substituted cyclopentadienes, (trimethylsilyl)tetramethylcyclopentadienide anion, C-electrophiles, alkylation, regioselectivity, 1,2,3,4-tetramethylfulvene, ^1H NMR spectroscopy, ^{13}C NMR spectroscopy, quantum-chemical calculations.

Organoelement derivatives of cyclopentadiene are of interest, to a great extent, because these compounds are initial for syntheses of different substituted cyclopentadienyl ligands widely used in organometallic chemistry. Among them, peralkylated ω-heteroelement-substituted cyclopentadienyl ligands are of particular importance, whose synthesis is still far from simplicity. Therefore, the development of new preparative approaches to syntheses of these compounds is rather urgent. One of the methods for their preparation is the alkylation of a (trimethylsilyl)tetramethylcyclopentadienide anion with appropriate C-electrophiles to form functionalized cyclopentadienylsilanes, which can further be directly used in syntheses of transition metal complexes. In this case, the main problem is the regioselectivity of alkylation. The attack of an electrophile can result in both the target 1,2,3,4,5-pentaalkyl-substituted derivatives and undesirable *gem*-dialkyl-substituted cyclopentadienes (Scheme 1), which are often the main products (for example, for the alkylation of the tetramethylcyclopentadienide[1]).

Scheme 1



R = Me (**2**), CH_2CH_2Cl (**3**)
RX = MeI, MeOTs, $ClCH_2CH_2Br$, $ClCH_2CH_2I$

The purpose of this work is to study the regioselectivity of the reaction of lithium (trimethylsilyl)tetramethylcyclopentadienide $C_5Me_4SiMe_3^-Li^+$ (**1**) with C-electrophiles (alkyl halides and formaldehyde) and to elucidate possibilities of its preparative application.

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In addition, it seemed of interest to substantiate the experimental data obtained in this work by quantum-chemical methods.

Results and Discussion

Reactions of salt 1 with electrophiles. We began to study the regioselectivity of alkylation of salt **1** from methylation with standard methylating agents (methyl iodide and methyl tosylate) in different ethereal solvents. It turned out that the reaction affords a mixture of isomeric pentamethylcyclopentadienylsilanes (**2a—c**) (see Scheme 1). The reactions with 1-bromo-2-chloroethane and 2-chloro-1-iodoethane were performed under the found optimal conditions (*i.e.*, favoring the formation of isomers of type **a**). In the case of predominant attack at the silylated C atom, these reactions could produce [1-(2-chloroethyl)tetramethylcyclopentadien-1-yl]silane (**3a**) which is practically important.

The structures of the resulting isomers and the composition of reaction mixtures were established by ^1H and ^{13}C NMR spectroscopies. In this respect, *gem*-dialkyl-substituted isomers **b** and **c** are the most complicated examples. Signals in the ^1H NMR spectra were assigned on the basis of measurements of the NOE difference spectra (when signals of Me groups are saturated, the NOE is observed only for adjacent Me groups or CH_2 moieties); the relative intensity of signals corresponding to the content of isomers in the mixture was also taken into account. The noticeable homoallyl interaction between Me groups through the double bond ($^5J_{H,H} = 1.2$ Hz) partially simplifies the task of assignment. When analyzing the ^{13}C NMR spectra, we also took into account the relative intensity of signals; in addition, in the case of isomers **3b** and **3c**, we took into account the $^1J_{C,H}$ values in the ^{13}C NMR spectrum obtained without proton decoupling. Signals of allylic isomers of type **a** are easily discernible in all spectra, because they are broadened due to [1,2]-elementotropic shifts,[2] which are impossible in *gem*-dialkyl-substituted isomers of types **b** and **c**. For compound **3a**, the presence of all three possible (by position of the Si atom) isomers in the mixture, along with the broadening of the signals and a low relative content (7—8%, see below), makes it possible to observe in the ^1H и ^{13}C spectra only signals of the $SiMe_3$ groups, which were used for integration.

The results of experimental studies on the regioselectivity of alkylation of salt **1** are presented in Table 1. In all cases, the reactions afford only the products shown in Scheme 1. Admixture signals in the spectra of the reaction mixtures belonged only to the starting solvent and alkylating agent. As can be seen from the data in Table 1, the maximum content of target isomer **2a** in the mixture is achieved upon methylation when MeI is used in n-donor solvents (THF and 1,2-dimethoxyethane (DME)). On going from MeI to MeOTs, the relative content of **2a** in a mixture decreases by approximately 10%. At the same time, in weakly solvating Et_2O the reaction produces almost exclusively *gem*-dimethyl-substituted cyclopentadienes **2b**,**c**. The data for alkylation in Et_2O with a small amount of THF (10 vol.%) to accelerate the reaction are presented in Table 1. When the reaction is performed in pure Et_2O, the ratio of products is almost the same as that with a THF additive; however, to obtain an appropriate overall yield, the duration of the reaction should be at least fortnight at room temperature. In this case, the reaction is heterogeneous in fact, because the starting salt is almost insoluble in Et_2O.

Alkylation with bulkier alkylating agents ($ClCH_2CH_2Br$ and $ClCH_2CH_2I$) resulted in a dramatic decrease in the yield (7—8% in a mixture) of target isomers **3a** even in THF, where the best result of methylation was achieved. For verification, the reaction was reproduced in an Et_2O—THF mixture (10 vol.% THF). Under these conditions, isomer **3a** does not form at all.

From our viewpoint, the results obtained can be explained as follows. The electron density distribution in the anion of salt **1** favors the attack of an electrophile at the C atom linked to the Si atom. Its maximum is arranged at this atom (for the results of quantum-chemical calculations, see below). However, the direction of the reaction is determined by the competition of electronic and steric factors caused by a larger volume of the trimethylsilyl substituent. An increase in the substituent

Table 1. Ratios of isomeric products (**a**/(**a** + **b** + **c**) and **b**/**c**) of the alkylation of $C_5Me_4SiMe_3Li$ (**1**) in different solvents

RX	THF		DME		Et_2O—THF (10 vol.%)*	
	a/(**a** + **b** + **c**)	**b**/**c**	**a**/(**a** + **b** + **c**)	**b**/**c**	**a**/(**a** + **b** + **c**)	**b**/**c**
MeI	0.62	0.83	0.53	0.74	0.05	0.38
MeOTs	0.50	0.42	0.44	0.41	—	—
$ClCH_2CH_2Br$	0.07	0.61	—	—	0	0.41
$ClCH_2CH_2I$	0.08	0.72	—	—	—	—

* The reaction occurs very slowly in pure Et_2O.

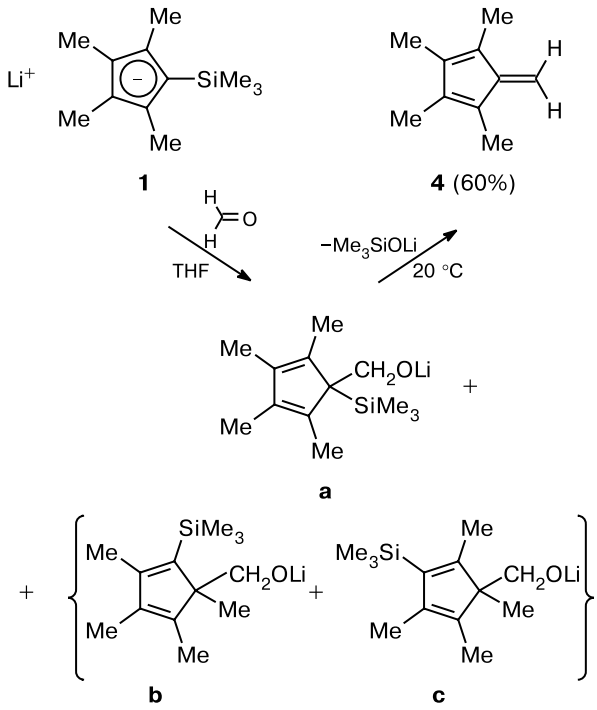
volume in an electrophile from methyl to 2-chloroethyl results in a dramatic change in the regioselectivity of alkylation and formation of almost exclusively *gem*-dialkyl-substituted products **b** and **c**. The presence of an electron-withdrawing Cl atom in the β-position to the reaction center can hardly affect considerably the regioselectivity of alkylation of **1**.

The same sharp change in the regioselectivity on going from strongly solvating solvents (THF, DME) to weakly solvating Et_2O is explained, most likely, by different states of the anion of salt **1** in these solvents. In THF and DME, salt **1** exists, most probably, as solvate-separate ion pairs, and its structure is close to that of a "pure" anion. In ether the equilibrium is shifted toward contact ion pairs and their aggregates.[3] It is most likely that in the transition state the Li^+ cation shifts to the C atom of the ring with the maximum electron density (*i.e.*, to the silylated C atom) and, thus, shields it from the attack by an electrophile. Due to this, even spatially non-hindered electrophiles have to attack positions of the cyclopentadienyl ring remote from the trimethylsilyl substituent.

Some regularities concerning the ratio of *gem*-dialkyl-substituted products **b** and **c** in the reaction mixture can be mentioned. As can be seen from the data in Table 1, in all reactions the content of isomer **c** is higher than that of isomer **b**. The best agreement with the computational data (see below) is observed for the reaction of the anion of salt **1** with MeI in THF. On going from an electrophile with a less bulky leaving group (MeI) to an electrophile with a bulkier leaving group (MeOTs) in both THF and DME, the content of isomer **c** increases considerably over **b**. A similar tendency is observed on going to weakly solvating Et_2O. These facts can indirectly confirm that both the Li^+ cation and leaving group are involved in the transition state, regardless of solvent.

As follows from the experimental data presented above, a small volume of the electrophilic carbonyl reactant is determining for the predominant attack of salt **1** to the C atom bound to the Si atom. Therefore, formaldehyde, which is less sterically hindered than MeI, was chosen as an electrophilic agent. The reaction of salt **1** was carried out with excess formaldehyde in THF. The attack of salt **1** at the C atom of the carbonyl group affords three intermediate isomeric lithium alkoxides (**a**, **b**, and **c**) (Scheme 2), the first of which eliminates Me_3SiOLi even at room temperature to give 1,2,3,4-tetramethylfulvene **4** in a good yield. In this case, the ^1H NMR spectrum of the reaction mixture exhibits characteristic signals of the alkoxide OCH_2 groups in a region of δ 3.2—3.5. The target fulvene can easily be separated from side lithium alkoxides **b** and **c**. The overall yield of compound **4** in this reaction (60%) indicates that its regioselectivity is close to that observed for the alkylation of salt **1** with methyl iodide. Thus, the reaction of salt **1** with formaldehyde can be an appropriate alternative for the already known methods for the preparation of 1,2,3,4-tetramethylfulvene,[4—8] the most convenient of which is the recently developed synthesis[8] based on the hydride transfer from the pentamethylcyclopentadienide anion to triphenylchloromethane.

Scheme 2



Quantum-chemical calculation of the anion of salt 1. The ground state of the $C_5Me_4SiMe_3^-$ anion was calculated by the quantum-chemical methods RHF and DFT (RMPW1PW91)[9] in the valence-split basis set 6-311+G(d,p) with addition of diffuse and polarization functions using the GAUSSIAN-98W program.[10] To decrease the computational costs, the geometry of the anion was optimized in a conformation possessing the maximum possible symmetry (C_s). Wave functions for this conformation were tested for stability and used further to determine charges according to Bader[11] by integration over atomic basins using the AIMPAC program package.[12]* The results of calculations are presented in Table 2.

It can be seen from Table 2 that both the DFT and RHF methods provide almost the same conclusions on the regioselectivity of alkylation. Higher differences (~5%) are observed for the case of orbital control; however, they also are within the error of the method. It follows from the computational data that the "charge-controlled" reaction should occur predominantly at the silylated C atom, while

* The program package is available free of charge at http://www.chemistry.mcmaster.ca/aimpac/download/aimpac.zip

Table 2. Total charges on atoms (q) according to Bader and the sum of squared orbital coefficients of HOMO (wave functions RHF and RMPW1PW91 6-311+G(d,p)) in the competitive positions of the $C_5Me_4SiMe_3^-$ ring

Atom	$-q$/e		Sum of squared orbital coefficients of HOMO[a]		Estimated ratio of alkylation products			
					charge control		orbital control	
	RHF	DFT	RHF	DFT	RHF	DFT	RHF	DFT
C(1)	0.9853	0.9321	1.5708	1.3884	1.00 (78.6%)	1.00 (78.0%)	1.00 (37.7%)	1.00 (33.0%)
C(2) + C(5)	0.1143[b]	0.1165[b]	1.1701[c]	1.4236[c]	0.12 (9.1%)	0.12 (9.7%)	0.74 (28.1%)	1.03 (33.8%)
C(3) + C(4)	0.1539[b]	0.1465[b]	1.4263[c]	1.4006[c]	0.16 (12.3%)	0.16 (12.3%)	0.91 (34.2%)	1.01 (33.2%)

[a] The coefficients at the AO of two close in energy HOMO ($\Delta E < 0.005$ eV) are taken into account.
[b] The total charges are summed up for pairs of equivalent atoms C(2), C(5) and C(3), C(4).
[c] The squared orbital coefficients at the AO are summed up for pairs of equivalent atoms C(2), C(5) and C(3), C(4).

in the case of "orbital" control, the attack to this atom is only by ~2 times preferential than that any other atom of the ring. Taking into account statistical factors for orbital control, isomeric products should be produced in approximately equal amounts. A comparison with the experimental data shows that non-hindered alkyl halide (MeI) and formaldehyde react with salt **1** in THF according to the "hard" type (*i.e.*, we deal with the case of "charge" control).

Thus, the regioselectivity of the reaction of C-electrophiles with lithium (trimethylsilyl)tetramethylcyclopentadienide is determined by three factors: electron density distribution in molecule **1**, steric hindrance of the electrophilic agent, and solvating ability of the medium. The first factor favors the attack of an electrophile at the C atom linked yo the Si atom, and the interaction occurs *via* the "hard" type (a case of "charge control"), which is confirmed by quantum-chemical calculations. At the same time, an increase in the electrophile volume and a decrease in the solvating ability of an ethereal solvent change the regioselectivity of the reaction, and the main products, in this case, are *gem*-dialkyl-substituted cyclopentadienes.

Experimental

The syntheses of trimethyl-(2,3,4,5-tetramethylcyclopenta-2,4-dien-1-yl)silane and its lithium salt, all alkylation reactions, and preparation of samples for NMR spectra were carried out in an all-sealed evacuated Schlenk-type glassware. 1,2,3,4-Tetramethylfulvene was synthesized under additionally purified argon (columns packed with KOH, P_2O_5, and a solution of sodium benzophenone ketyl in diglyme). Lithium tetramethylcyclopentadienide was prepared by the treatment of tetramethylcyclopentadiene[13] in THF with a solution of *n*-butyllithium in hexane and purified as a solid salt by multiple washings on a filter with THF and then with Et_2O. 2-Chloro-1-iodoethane was obtained using a procedure similar to a described method[14] by the reaction of $KICl_2$ with ethylene in CH_2Cl_2. Commercially available 1-bromo-2-chloroethane, methyl tosylate, methyl iodide, and paraform were used. Solvents and alkylating agents were dried using standard procedures.[15] ^1H and ^{13}C NMR spectra were recorded on a Varian VXR-400 spectrometer (400 and 100 MHz, respectively) at 25 °C.

Trimethyl-(2,3,4,5-tetramethylcyclopenta-2,4-dien-1-yl)silane (5) was synthesized according to a modified procedure.[16] Trimethylchlorosilane (15.12 g, 139.2 mmol) was added under stirring to a suspension of lithuim tetramethylcyclopentadienide (17.21 g, 134.3 mmol) in absolute THF (120 mL) at 0 °C. The temperature of the reaction mixture was brought to room temperature (~20 °C). The reaction mixture was stirred for 1 h (after 30 min, the whole precipitate virtually dissolved). The solvent was removed *in vacuo*, and the resulting oily substance was extracted with pentane to separate lithium chloride. After pentane was removed, the product was distilled *in vacuo* (52 °C, 1 Torr). Silane **5** (colorless viscous liquid) was obtained in 75% yield (19.58 g). ^1H NMR (C_6D_6), δ: −0.04 (s, 9 H, $SiMe_3$); 1.80, 1.90 (both s, 6 H each, CMe); 2.67 (s, 1 H, CH). $^{13}C\{^1H\}$ NMR (C_6D_6), δ: −1.56 ($SiMe_3$); 11.31, 14.66 ($C\underline{C}H_3$); 55.38 (CH); 132.92, 135.45 ($\underline{C}$Me).

Lithium (trimethylsilyl)tetramethylcyclopentadienide (1). A 2.16 *M* solution of Bu^nLi (26 mL, 56 mmol) in hexane was added under stirring to a solution of silane **5** (10.22 g, 52.6 mmol) in absolute THF (150 mL) at −20 °C. The temperature of the reaction mixture was brought to room temperature (~20 °C). The reaction mixture was stirred for 2 h. The solvent was removed *in vacuo*, and the residue was washed with absolute Et_2O (2×80 mL) and dried in a high vacuum. Compound **1** was obtained as a white powder in 94% yield (9.90 g). ^1H NMR (THF-d_8), δ: 0.13 (s, 9 H, $SiMe_3$); 1.83, 1.94 (both s, 6 H each, CMe). $^{13}C\{^1H\}$ NMR (THF-d_8), δ: 3.97 ($SiMe_3$); 11.66, 14.60 ($C\underline{C}H_3$); 100.8 (br.s, $\underline{C}SiMe_3$); 112.38, 116.52 ($\underline{C}$Me).

Trimethyl(pentamethylcyclopentadienyl)silane (mixture of isomers 2a—c). Reaction of salt **1** with methyl iodide in THF. Methyl iodide (210 mg, 1.5 mmol) was added to a solution of salt **1** (200 mg, 1 mmol) in THF (5 mL) at −50 °C. The temperature of the reaction mixture was brought to room temperature (~20 °C). The reaction mixture was stirred for 2 h. The solvent and excess MeI were distilled off *in vacuo*, the residue was dissolved in C_6D_6 and placed into an NMR tube, and the tube was sealed.

The reactions of salt **1** with MeI in DME and an Et_2O—THF (10 vol.%) mixture and the reactions of **1** with TsOMe in THF and DME were carried out similarly. In all experiments, a 1.5-fold excess of an alkylating agent was used. A weighed sample of TsOMe was preliminarily dissolved in 2 mL of the corresponding solvent. ^1H NMR (C_6D_6), δ: −0.11 (s, $SiMe_3$ (**2a**));

0.28 (s, $SiMe_3$ (**2c**)); 0.29 (s, $SiMe_3$ (**2b**)); 0.86 (s, MeC(5) (**2c**)); 1.06 (s, MeC(5) (**2b**)); 1.17 (br.s, MeC(5) (**2a**)); 1.65 (br.s, MeC(3), MeC(4), (**2b**)); 1.69 (br.s, MeC(4) (**2c**)); 1.79 (br.s, MeC(1), MeC(2), MeC(3), MeC(4) (**2a**)); 1.88 (br.s, MeC(3) (**2c**), MeC(2) (**2b**)); 1.89 (s, MeC(1) (**2c**)). $^{13}C\{^1H\}$ NMR (C_6D_6), δ: −2.70 ($SiMe_3$ (**2a**)); 1.70 ($SiMe_3$ (**2b,c**)); 9.78, 12.98, 14.55 ($\underline{C}H_3C(1)$, $\underline{C}H_3C(3)$, $\underline{C}H_3C(4)$ (**2c**)); 9.89, 10.96, 15.01 ($\underline{C}H_3C(2)$, $\underline{C}H_3C(3)$, $\underline{C}H_3C(4)$ (**2b**)); 11.2, 12.5 (both br.s, $\underline{C}H_3C(1)$, $\underline{C}H_3C(2)$, $\underline{C}H_3C(3)$, $\underline{C}H_3C(4)$ (**2a**)); 13.7 (br.s, $\underline{C}H_3C(5)$ (**2a**)); 21.95 ($\underline{C}H_3C(5)$ (**2c**)); 22.26 ($\underline{C}H_3C(5)$ (**2b**)); 53.7 (br.s, C(5) (**2a**)); 55.51 (C(5) (**2c**)); 56.89 (C(5) (**2b**)); 132.94, 145.31, 150.37, 151.17 (C(1), C(2), C(3), C(4) (**2b**)); 134.31, 135.05, 142.64, 162.19 (C(1), C(2), C(3), C(4) (**2c**)); 134.7, 138.1 (both br.s, C(1), C(2), C(3), C(4) (**2a**)).

Trimethyl(tetramethyl(2-chloroethyl)cyclopentadienyl)silane (mixture of isomers 3a—c). A procedure of alkylation of lithium salt **1** with 1-bromo-2-chloroethane and 2-chloro-1-iodoethane in THF and an Et_2O—THF (10 vol.%) mixture is similar to that described above for alkylation with methyl iodide. ^1H NMR (C_6D_6), δ: −0.23, −0.17 (both br.s, $SiMe_3$ (**3a**)); 0.19 (s, $SiMe_3$ (**3c**)); 0.20 (s, $SiMe_3$ (**3b**)); 0.72 (s, MeC(5) (**3c**)); 0.92 (s, MeC(5) (**3b**)); 1.43 (q, MeC(4), $^5J_{H,H}$ = 1.2 Hz (**3b**)); 1.47 (q, MeC(4), $^5J_{H,H}$ = 1.2 Hz (**3c**)); 1.53 (q, MeC(3), $^5J_{H,H}$ = 1.2 Hz (**3b**)); 1.67 (s, MeC(1) (**3c**)); 1.76 (q, MeC(3), $^5J_{H,H}$ = 1.2 Hz (**3c**)); 1.78 (s, MeC(2) (**3b**)); 1.83 (m, $C\underline{H}_2CH_2Cl$ (**3c**)); 1.94, 2.27 (both m, $C\underline{H}_2CH_2Cl$ (**3b**)); 2.75 (m, CH_2Cl (**3c**)); 2.77, 2.93 (both m, CH_2Cl (**3b**)). ^{13}C NMR (C_6D_6), δ: −2.9 (br.q, $SiMe_3$, $^1J_{C,H}$ = 120 Hz (**3a**)); 1.25 (q, $SiMe_3$, $^1J_{C,H}$ = 118 Hz (**3b**)); 1.49 (q, $SiMe_3$, $^1J_{C,H}$ = 118 Hz (**3c**)); 9.56, 12.78, 14.37 (all q, $\underline{C}H_3C(1)$, $\underline{C}H_3C(3)$, $\underline{C}H_3C(4)$, $^1J_{C,H}$ = 125 Hz (**3c**)); 9.76, 10.76, 14.91 (all q, $\underline{C}H_3C(2)$, $\underline{C}H_3C(3)$, $\underline{C}H_3C(4)$, $^1J_{C,H}$ = 125 Hz (**3b**)); 21.87 (q, $\underline{C}H_3C(5)$, $^1J_{C,H}$ = 127 Hz (**3c**)); 22.34 (q, $\underline{C}H_3C(5)$, $^1J_{C,H}$ = 126 Hz (**3b**)); 38.40 (t, $\underline{C}H_2CH_2Cl$, $^1J_{C,H}$ = 129 Hz (**3c**)); 39.15 (t, $\underline{C}H_2CH_2Cl$, $^1J_{C,H}$ = 129 Hz (**3b**)); 40.54 (t, CH_2Cl, $^1J_{C,H}$ = 149 Hz (**3c**)); 41.03 (t, CH_2Cl, $^1J_{C,H}$ = 149 Hz (**3b**)); 58.80 (s, C(5) (**3c**)); 60.23 (s, C(5) (**3b**)); 135.33, 136.75, 139.22, 158.56 (all s, C(1), C(2), C(3), C(4) (**3c**)); 138.07, 142.08, 147.12, 153.26 (all s, C(1), C(2), C(3), C(4) (**3b**)).

1,2,3,4-Tetramethylfulvene (4). Paraform (3.50 g, 116.4 mmol), which was preliminarily stored for a long time *in vacuo* above P_2O_5, was depolymerized in an argon flow on heating, and the formed formaldehyde was trapped at −30 °C in absolute THF (100 mL). A solution of salt **1** (7.77 g, 38.8 mmol) in THF (80 mL) was added to the resulting solution under stirring and cooling to −20 °C for 1 h. The temperature of the reaction mixture was brought to room temperature (~20 °C). The reaction mixture was left to stand for ~14 h. The resulting orange solution was filtered through a column with silica gel (0.063—0.200 mm, 10-cm layer) under argon to separate side lithium alkoxides, and the solvent was distilled off under reduced pressure (120 Torr). The product (orange-red oil) was distilled *in vacuo* (35—40 °C, 1 Torr). Compound **4** was obtained as an orange-red oil in 60% yield (3.12 g). The ^1H and ^{13}C NMR spectra coincide with the previously published spectra.[7,8]

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