New photochromic diarylethenes including P and Si atoms

Lahoussine Bougdid, Andre Samat and Corinne Moustrou*

Received (in Montpellier, France) 20th January 2009, Accepted 25th February 2009
First published as an Advance Article on the web 6th April 2009
DOI: 10.1039/b901277j

The preparation of new photochromic diarylcyclopentenes including silicon or phosphorus atom in the pentatomic cycle is described. Starting from butadienes substituted in 2 and 3 positions by thienyl or benzothienyl groups, the targeted molecules have been obtained through a three-step convergent synthesis with relatively good yield. These original structures open a novel area of investigations for this family of compounds which is known for promising applications in the fields of optoelectronic devices and optical memories.

Introduction

In the last decade, interest toward photochromic diarylethenes, involving a ring closure/opening electrocyclic isomerisation, has been largely developed due to their thermal irreversibility, sensitivity and fatigue resistance.[1,2] These intrinsic properties make diarylethenes and particularly bis(thienyl)perfluorocyclopentenes, highly promising for various applications. Indeed, besides the reversible change of colour, additional potentialities for technological applications could be offered by this family of compounds such as the preparation of light-triggered switching devices[3–5] and optical molecular memories.[6–9] In this regard, a high difference of fluorescence response between the open and closed forms is essential for the design of non-erasable readout systems.[2,10,11] Unfortunately this emission difference is generally very weak for the parent compounds and the linkage of a fluorophore unit is often necessary.[2,12–15]

We assumed that a modification of the structure of the pentatomic cycle could induce this kind of behaviour. Many attempts have been performed to introduce heteroatoms (O, S, N) in the cycle[16–19] but never with silicon or phosphorus atoms.

In this work, we describe the synthetic strategies used to build the target molecules **4** and **5** (Scheme 1).

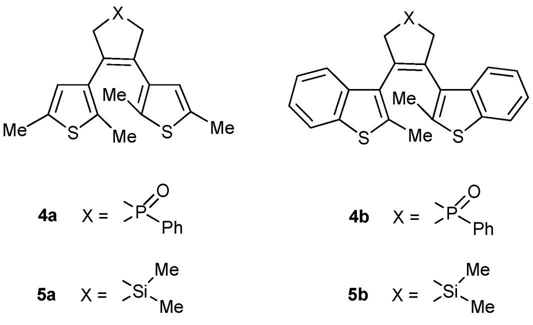
These latest compounds **4** and **5**, as described recently, exhibit very interesting optical properties, the open forms being fluorescent while the closed form is not fluorescent.[20]

Results and discussion

In the patent literature of 1953,[21] McCormack reported the first synthesis of a new class of heterocyclic system, referred to as phospholene oxide, through a versatile 1,4-cycloaddition of 1,3-dienes with dihaloarylphosphines or dihaloalkylphosphines (Scheme 2).

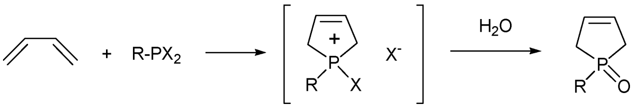
The highly reactive intermediate salts, were not isolated but readily hydrolyzed into the corresponding phospholene oxides. Several years later, this pioneering work of McCormack, has been reviewed in detail[22–24] and it was demonstrated that the McCormack protocol led in fact to a mixture of two regioisomers (Scheme 3).[25–28]

However, by selecting appropriate phosphorylated reactant and the experimental conditions,[29–32] it is possible to prepare selectively one regioisomer or the other, according to a very simple procedure. The cycloaddition reaction from the conjugated diene and the phosphorylated reactant is performed in an apolar solvent (C_5 or C_6 alkane) at room temperature for prolonged periods (days or weeks), in the presence of a polymerization inhibitor. Copper(II) stearate[33] is currently used. In order to reduce reaction time, cycloadditions can be performed in refluxing solvent but side reactions, especially polymerization constitute a serious problem. The structure of the adduct, but also the structure of the final products, are primary controlled by the nature of substituent on the phosphorus dichloride. A methyl substituent leads to phosphol-3-enes, while a phenyl group leads to phosphol-2-enes. The replacement of chloride by bromine in phosphorus dihalide gives the opposite selectivity. It is noteworthy that this general behaviour is true only for room-temperature conditions.[34] The hydrolysis conditions of the cycloadducts have a definite influence on the ratio of the two regioisomers. If the intermediate salt is simply added to water, with no control of high acidity, the product is largely or exclusively the 2-isomer. In contrast, the hydrolysis performed by addition to cold concentrated $NaHCO_3$ or dilute NaOH solution, contributes to the formation of the 3-isomer. The reaction of McCormack constitutes an efficient method for building of phosphorus-containing five-membered rings.

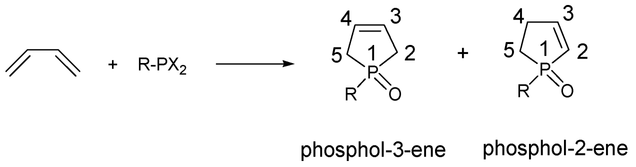


Scheme 1 Targeted diarylethenes.

CNRS, Aix-Marseille Université, CINAM-UPR3118, Campus de Luminy, Case 913, 13288, Marseille cedex 09, France.
E-mail: moustrou@cinam.univ-mrs.fr



Scheme 2 Synthesis of phospholene oxides by McCormack cycloaddition reaction.



Scheme 3 Regioselectivity of the McCormack cycloaddition reaction.

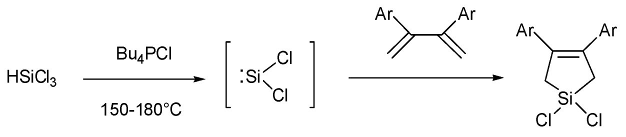
The same synthetic approach can be used to prepare the analogous silylated heterocycles.[35] In this case, silylene reactive intermediates[36,37] were involved. These latter are formed *via* the thermolysis[38–41] or the photolysis[42] of appropriate substrates. However, the high temperatures required for their formation, are incompatible with the stability of the photochromic moiety. The methodology recently reported by Jung *et al.*,[43,44] enables to overcome this difficulty, through phosphorus-induced silylene transfer (Scheme 4).

Synthesis of the new diarylethenes requires the preliminary preparation of the suitable dienes **1** and **2**. It is obvious that the preparation of these key intermediates must be optimal. Therefore, two methodologies were developed. The first one is a classic Kumada cross-coupling reaction starting from requisite vinyl halides (method 1).[45–47] In the second process, the cross-coupling is mediated with palladium from the propargyl carbonate **3** and the corresponding boronic acids (method 2).[48]

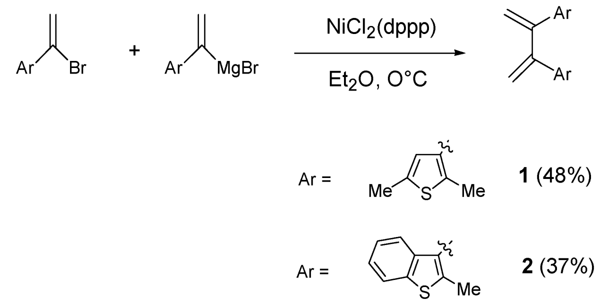
A Kumada coupling of 3-(α-bromovinyl)-2,5-dimethylthiophene (1 eq.) with its own Grignard reagent (1.5 eq.), in the presence of a catalytic amount of $NiCl_2$(dppp) ([1,3-bis(diphenylphosphino)propane]nickel(II) chloride) (5 mol%) in diethyl ether at room temperature, followed by acidic hydrolysis afforded the diene **1** in 48% isolated yield. In a similar way, the diene **2** was prepared in only 37% yield (Scheme 5).

Since the yields did not exceed 50%, we investigated the second cross-coupling methodology (Scheme 6).

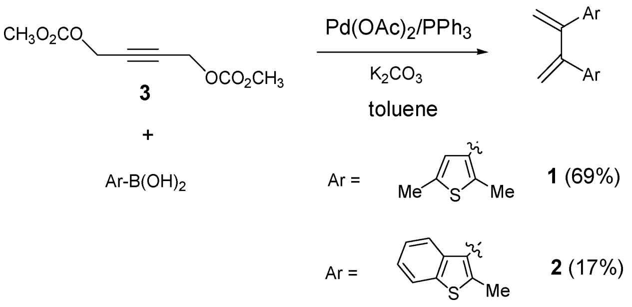
The cross-coupling of the dicarbonate **3** (1 eq.) with 2,5-dimethylthiophene-3-boronic acid (2.2 eq.) was carried out at room temperature in the presence of anhydrous K_2CO_3 (3 eq.), catalytic amounts of $Pd(OAc)_2$ (10 mol%), H_2O and PPh_3 (20 mol%) in toluene, gave the expected diene **1** in satisfying yield (69%). Disappointingly, the yield decreased dramatically for diene **2** (17%).



Scheme 4 Formation of silylene by Jung's methodology.



Scheme 5 Preparation of dienes **1** and **2** from vinyl halides (method 1).



Scheme 6 Preparation of dienes **1** and **2** from boronic acids (method 2).

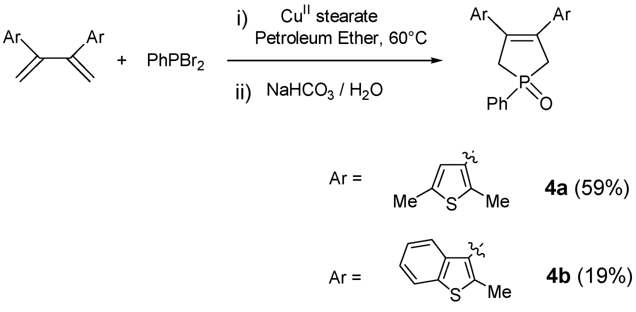
Concerning now the synthesis of the target diarylethenes:

(i) The synthesis of the phospholene oxides **4a** and **4b** was accomplished from McCormack 1,4-cycloaddition reaction as outlined in Scheme 7.[49]

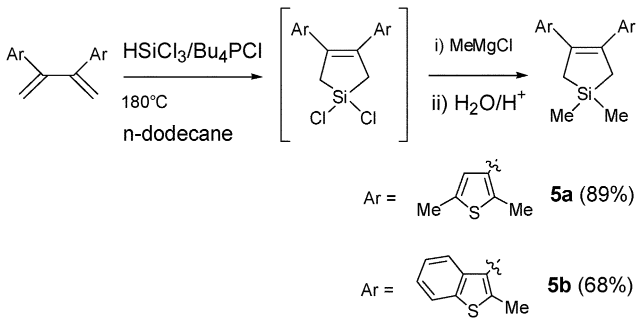
Dibromophosphine (1.25 eq.) reacted with the appropriate diene (1 eq.) in the presence of a catalytic amount of copper(II) stearate. The cycloaddition was carried out in petroleum ether (bp 60–80 °C) at 70 °C for 10 days under argon. The reaction was monitored by TLC and stopped when the starting diene was consumed. **4a** and **4b** were obtained in 59 and 19% yield, respectively.

(ii) Jung methodology was applied to prepare the silylated analogues, as shown in Scheme 8.

The reaction of the appropriate diene (1 eq.) with trichlorosilane (4 eq.) was investigated using a catalytic amount of tetrabutylphosphonium chloride (10 mol%) in *n*-dodecane at 180 °C for 10 h. The intermediate dichlorinated diarylethenes, which were not isolated, were further treated with the commercially available methylmagnesium chloride (12 eq.) at 0 °C, followed by acidic hydrolysis, to afford the desired silylated diarylethenes **5a** et **5b** in very good yields (89 and 68%, respectively).



Scheme 7 Synthesis of the phosphorylated diarylethenes **4a** and **4b**.



Scheme 8 Synthesis of the silylated diarylethenes **5a** and **5b**.

Conclusion

The preparation of dithienyl- or dibenzothienyl-cyclopentenes including a silicon or phosphorus atom has been successfully performed according to convenient convergent processes using butadienes substituted in 2 and 3 positions by thiophene or a benzothiophene rings. Experiments are in progress to extend the substitution of dibenzothienyl derivatives which are very interesting regarding the preliminary photochemical properties obtained otherwise.[20] For instance, compounds **4a** and **4b** are not fluorescent, whereas the corresponding closed forms **4b** and **5b** show fluorescence emission (quantum yield 0.002 at 570 nm and 0.003 at 575 nm, respectively).

Experimental

General remarks

Melting points were determined in capillary tubes on a Büchi 510 apparatus and are uncorrected. Nuclear magnetic resonance (^{1}H, ^{13}C and ^{31}P NMR) spectra were recorded on a Bruker AC250 (250, 62.5 and 101.25 MHz, respectively) spectrometer. Chemical shifts are reported in parts per million (δ) relative to the non-deuterated solvent peak. Coupling constants (J values) are expressed in hertz (Hz), and spin multiplicities are indicated by the following symbols: s (singlet), d (doublet) and m (multiplet). DEPT ^{13}C information is given in parenthesis as C, CH, CH_2 and CH_3. Elemental analyses were performed on a LECO-932-CNR analyzer. Column chromatography was carried out using silica gel 60 230-400 mesh (Merck & Co.). Routine thin layer chromatography (TLC) was effected by using precoated aluminium sheets (60 F254) with a 0.2 mm thickness (Aldrich Chemical Co.). The relative proportion of solvents in mixed chromatography solvents refers to the volume/volume ratio. All reactions were performed in standard glassware, which was dried for a minimum of 12 h in a oven at 140 °C.

Solvents and chemicals

Et_2O and THF were distilled from sodium benzophenone ketyl under argon immediately prior to use. Solvents were of analytical grade from commercial sources and were used as received. The petroleum ether used had a boiling range of 60–80 °C. $Pd(OAc)_2$ and $NiCl_2$(dppp) were commercially available from Strem, and were used as supplied. Butyne dicarbonate **3**,[50] dibromophenylphosphine[25,51] and copper(II) stearate[52] were prepared by known methods. Vinyl halides[53,54] and boronic acids[55–57] were synthesized according to usual procedures.

General methods for the preparation of dienes

Method 1. Mg turnings (1.59 g, 65.5 mmol) and dry diethyl ether (25 mL) were introduced successively to a flask equipped with a magnetic stirrer and a reflux condenser under argon flow. A solution of the appropriate vinyl halide (54.6 mmol) in dry Et_2O (15 mL) was added dropwise. The rate of addition was adjusted so as to maintain the reflux of the reaction mixture. After the addition was over, stirring was continued at room temperature for 1 h, the Grignard solution was transferred to the pressure-equalizing dropping funnel of a second apparatus *via* a cannula, and added dropwise over a period of 40 min to an ice-cooled solution of the appropriate vinyl halide (43.68 mmol), $NiCl_2$(dppp) (1.18 g, 2.18 mmol) in dry Et_2O (250 mL), while the reaction flask temperature was maintained below 5 °C. After completion of the addition, the ice-bath was removed. The resulting mixture was allowed to rise to room temperature, and stirring was continued overnight. After cooling (ice-bath), the reaction was quenched with 1.2 M aqueous hydrochloric acid (150 mL). The resulting mixture was filtered over a bed of Celite, which was carefully rinsed with Et_2O (2 × 10 mL). The separated aqueous layer was extracted with Et_2O (3 × 50 mL), and the combined organic solutions were washed with a saturated aqueous bicarbonate solution (3 × 50 mL) and water (3 × 50 mL), dried with $MgSO_4$, filtered and concentrated under reduced pressure. The resulting oily crude residue was subjected to column chromatography (SiO_2; eluent: cyclohexane) to afford the pure desired diene. The data for the individual compounds are given below.

Method 2. A 100 mL two-necked flask was charged with appropriate boronic acid (22 mmol), K_2CO_3 (4.15 g, 30 mmol), H_2O (4 mL) and toluene (20 mL), purged with argon and stirred for 15 min at room temperature. After the mixture was cooled to 0 °C, butyne dicarbonate (2.02 g, 10 mmol), $Pd(OAc)_2$ (224 mg, 1 mmol) and PPh_3 (524 mg, 2 mmol) were added subsequently. The system was flushed with argon. The heterogeneous mixture was then warmed to room temperature, and stirring was continued for 12 h. The crude reaction was filtered through a plug of Celite, the filter cake being thoroughly rinsed with benzene (2 × 10 mL). The organic layer was washed with saturated aqueous sodium bicarbonate solution (2 × 50 mL), water (2 × 50 mL) and brine (2 × 50 mL). The organic layer was dried over $MgSO_4$, filtered and concentrated to dryness under reduced pressure. The crude material was purified by column chromatography (SiO_2; eluent: *n*-hexane) to yield the expected diene. The data for the individual compounds are given below.

2,3-[Bis-(2,5-dimethylthien-3-yl)]buta-1,3-diene: 1. This compound was prepared by method (1): The Grignard reagent was formed from 3-(α-bromovinyl)-2,5-dimethylthiophene (11.85 g, 54.6 mmol) and magnesium (1.59 g, 65.5 mmol) and subsequent conventional Kumada coupling reaction of the latter with 3-(α-bromovinyl)-2,5-dimethylthiophene

(9.48 g, 43.68 mmol) gave the diene **1** in 48% (5.75 g, 20.95 mmol), as white crystals.

This compound was also obtained by method (2), from 2,5-dimethylthiophene-3-boronic acid (3.43 g, 22 mmol) in 69% yield (1.89 g, 6.9 mmol).

Mp 36 °C; ^{1}H NMR (250 MHz, $CDCl_3$) δ 6.45 (s, 2H), 5.06 (d, J = 1.1 Hz, 2H), 5.02 (d, J = 1.1 Hz, 2H), 2.33 (s, 6H), 2.24 (s, 6H); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 144.3 (2 × C), 137.5 (2 × C), 134.9 (2 × C), 132.8 (2 × C), 127.6 (2 × –CH═), 118.3 (2 × CH_2═), 15.2 (2 × CH_3–), 13.9 (2 × CH_3–). Anal. Calc. for $C_{16}H_{18}S_2$: C, 70.02; H, 6.61. Found: C, 69.92; H 6.71%.

2,3-[Bis(2-methylbenzo[b]thiophen-3-yl)]buta-1,3-diene: 2. This compound was prepared by method (1): The Grignard reagent was formed from 3-(α-bromovinyl)-2-methylbenzo[*b*]thiophene (13.82 g, 54.6 mmol) and magnesium (1.59 g, 65.5 mmol), and subsequent conventional Kumada coupling reaction of the latter with 3-(α-bromovinyl)-2-methylbenzo[*b*]thiophene (11.06 g, 43.68 mmol) gave the diene **2** in 37% yield (5.6 g, 16.16 mmol), as a white powder.

This compound was also obtained by method (2), from 2-methylbenzo[b]thiophene-3-boronic acid (4.22 g, 22 mmol) in 15% yield (519 mg, 1.5 mmol).

Mp 156 °C; ^{1}H NMR (250 MHz, $CDCl_3$) δ 7.73 (d, J = 7.5 Hz, 2H), 7.50 (d, J = 7.5 Hz, 2H), 7.40–7.15 (m, 4H), 5.17 (d, J = 1.1 Hz, 2H), 5.09 (d, J = 1.1 Hz, 2H), 2.50 (s, 6H); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 141.5 (2 × C), 140.6 (2 × C), 138.4 (2 × C), 136.5 (2 × C), 132.6 (2 × C), 124.2 (2 × –CH═), 123.7 (2 × –CH═), 122.4 (2 × –CH═), 122.0 (2 × –CH═), 120.9 (2 × CH_2═), 14.6 (2 × CH_3–). Anal. Calc. for $C_{22}H_{18}S_2$: C, 76.26; H, 5.24. Found: C, 76.31; H, 5.19%.

General method (3) for the synthesis of phosphorylated diarylethenes. A round-bottomed flask, equipped with a magnetic stirrer, was charged with the appropriate diene (2.42 mmol), dibromophenylphosphine (812 mg, 3.03 mmol) and copper(II) stearate (5 mg) in petroleum ether (bp 60–80 °C), 10 mL), purged with argon and stirred for 10 days in an oil-bath at 70 °C. The progress of the reaction was monitored by TLC (pentane–diethyl ether, 1 : 1). After complete disappearance of the diene, the reaction mixture was allowed to come to ambient temperature, and was quenched with saturated aqueous sodium bicarbonate solution (15 mL). The organic layer was separated and the aqueous layer was extracted with dichloromethane (4 × 15 mL). The combined organic extracts were dried with $MgSO_4$, filtered, and then concentrated under vacuum. The crude residue was purified by column chromatography (SiO_2; cyclohexane–AcOEt gradient 100 : 0 to 50 : 50) to provide the pure expected phosphorylated diarylethenes. The data for the individual compounds are given below.

3,4-Bis(2,5-dimethylthien-3-yl)-1-phenyl-2,5-dihydrophosphole 1-oxide: 4a. This compound was obtained by general method (3), starting from 2,3-[bis(2,5-dimethylthien-3-yl)]buta-1,3-diene (664 mg, 2.42 mmol). The product was isolated as a pale yellow powder (569 mg, 1.43 mmol, 59%).

Mp 119 °C; ^{1}H NMR (250 MHz, $CDCl_3$) δ 7.77–7.62 (m, 2H), 7.52–7.39 (m, 3H), 6.32 (s, 1H), 6.31 (s, 1H), 3.30 (dd, J_{HP} = 15.0 Hz, J = 17.5 Hz, 2H), 3.03 (dd, J_{HP} = 8.9 Hz, J = 17.5 Hz, 2H), 2.27 (s, 6H), 1.80 (s, 6H); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 135.9 (2 × C), 133.7 (C), 134.6 (C), 134.4 (C), 133.6 (d, J_{PC} = 93.7 Hz, C), 133.5 (2 × C), 132.2 (d, J_{PC} = 2.75 Hz, –CH═), 130.9 (C), 130.7 (C), 129.6 (d, J_{PC} = 9.7 Hz, 2 × –CH═), 128.9 (d, J_{PC} = 11.5 Hz, 2 × –CH═), 125.3 (2 × –CH═), 39.6 (d, J_{PC} = 66.1 Hz, 2 × –CH_2–), 15.2 (2 × CH_3–), 14.2 (2 × CH_3–); ^{31}P NMR (101.25 MHz, $CDCl_3$) δ 50.45. Anal. Calc. for $C_{22}H_{23}OPS_2$: C, 66.30; H, 5.82; S, 16.09; P, 7.77. Found: C, 66.21; H, 5.91; S, 16.17; P, 7.64%.

3,4-Bis(2-methylbenzo[*b*]thiophen-3-yl)-1-phenyl-2,5-dihydrophosphole 1-oxide: 4b. This compound was obtained by general method (3), starting from 2,3-[bis(2-methylbenzo[b]thiophen-3-yl)]buta-1,3-diene (838 mg, 2.42 mmol). The product was isolated as a yellowish solid (217 mg, 0.46 mmol, 19%). ^{1}H NMR (250 MHz, $CDCl_3$) δ 8.01–7.86 (m, 2H), 7.68–7.45 (m, 5H), 7.37–6.97 (m, 6H), 3.51 (dd, J = 16.3 Hz, J = 18.5 MHz, 2H), 3.13 (dd, J = 7.11 Hz, J = 18.3 Hz, 2H), 1.85 (s, 3H), 1.78 (s, 3H); ^{31}P NMR (101.25 MHz, $CDCl_3$) δ 49.43. Anal. Calc. for $C_{28}H_{23}OPS_2$: C, 71.46; H, 4.93; S, 13.63; P, 6.58. Found: C, 71.33; H, 4.87; S, 13.58; P, 6.52%.

General method (4) for the synthesis of silylated diarylethenes. An oven-dried resealable pressure tube containing a stir bar, was charged with the appropriate diene (1 mmol), trichlorosilane (542 mg, 4 mmol), tetrabutylphosphonium chloride (29.5 mg, 0.1 mmol) and *n*-dodecane (2 mL), purged with argon, and placed in a preheated oil-bath at 180 °C for 10 h. The reaction mixture was cooled to 0 °C and anhydrous THF (5 mL) was added, followed by a 3 M solution of methylmagnesium chloride in THF (4 mL, 12 mmol) with vigorous stirring. The resulting mixture was stirred at room temperature for 1 h. The reaction was quenched with 1 M aqueous hydrochloric acid (15 mL), and extracted with Et_2O (3 × 15 mL). The combined organic layers were dried over $MgSO_4$, filtered and concentrated under reduced pressure. The crude residue was purified by column chromatography (SiO_2; eluent: *n*-hexane) to furnish the pure expected diarylethene.

The data for the individual compounds are given below.

3,4-Bis(2,5-dimethylthien-3-yl)-1,1-dimethyl-2,5-dihydro-1*H*-silole: 5a. This compound was obtained by general method (4), starting from 2,3-[bis(2,5-dimethylthien-3-yl)]buta-1,3-diene (274 mg, 1 mmol). The product was isolated as white crystals (296 mg, 0.89 mmol, 89%).

Mp 103 °C; ^{1}H NMR (250 MHz, $CDCl_3$) δ 6.45 (s, 2H), 2.40 (s, 6H), 1.91 (s, 6H), 1.51 (s, 4H), 0.33 (s, 6H); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 141.6 (2 × C), 136.7 (2 × C), 136.5 (2 × C), 133.1 (2 × C), 128.7 (2 × –CH═), 29.2 (–CH_2–), 27.8 (–CH_2–), 17.4 (2 × CH_3–), 16.3 (2 × CH_3–), −0.01 (2 × CH_3–). Anal. Calc. for $C_{18}H_{24}S_2Si$: C, 65.00; H, 7.27; S, 19.28. Found: C, 65.12; H, 7.17; S, 19.31%.

3,4-Bis(2-methylbenzo[b]thiophen-3-yl)-1,1-dimethyl-2,5-dihydro-1*H*-silole: 5b. This compound was obtained by general method (4), starting from 2,3-[bis(2-methylbenzo[*b*]thiophen-3-yl)]buta-1,3-diene (346 mg, 1 mmol). The product was isolated as white spangles (275 mg, 0.68 mmol, 68%).

Mp 82 °C; ^{1}H NMR (250 MHz, $CDCl_3$) δ 7.60–6.70 (m, 8H), 2.12 (s, 4H), 1.62 (s, 6H), 0.24 (s, 6H); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 141.6 ($2 \times$ C), 140.4 ($2 \times$ C), 139.1 ($2 \times$ C), 137.1 ($2 \times$ C), 135.8 ($2 \times$ C), 125.7 ($2 \times$ –CH=), 125.2 ($2 \times$ –CH=), 124.6 ($2 \times$ –CH=), 124.2 ($2 \times$ –CH=), 26.9 ($2 \times$ $-CH_2-$), 17.3 ($2 \times$ CH_3-), −0.01 ($2 \times$ CH_3-). Anal. Calc. for $C_{24}H_{24}S_2Si$: C, 71.23; H, 5.98; S, 15.85. Found: C, 71.15; H, 5.89; S, 15.89%.

References

1 M. Irie, *Pure Appl. Chem.*, 1996, **68**, 1367.
2 M. Irie, *Chem. Rev.*, 2000, **100**, 1685.
3 B. L. Feringa, *J. Org. Chem.*, 2007, **72**, 6635.
4 M. Irie, in *Molecular Switches*, ed. B. L. Feringa, Wiley, Weinheim, 2001, pp. 37–62.
5 D. Sud, T. B. Norsten and N. R. Branda, *Angew. Chem., Int. Ed.*, 2005, **44**, 2.
6 M. Irie, *Hikari Araiansu*, 2006, **17**, 6.
7 C. C. Corredor, Z. L. Huang, K. D. Belfield, A. R. Morales and M. V. Bondar, *Chem. Mater.*, 2007, **19**, 5165.
8 T. J. Wigglesworth and N. R. Branda, *Adv. Mater.*, 2004, **16**, 123.
9 H. Tian and Y. Feng, *J. Mater. Chem.*, 2008, **18**, 1617.
10 K. Matsuda and M. Irie, *J. Photochem. Photobiol., C*, 2004, **5**, 169.
11 F. A. Alvaro and J. M. Lehn, *Chem.–Eur. J.*, 1999, **5**, 3285.
12 H. Tian and S. Yang, *Chem. Soc. Rev.*, 2004, **33**, 85.
13 T. Kawai, T. Sasaki and M. Irie, *Chem. Commun.*, 2001, 711.
14 H. Cho and E. Kim, *Macromolecules*, 2002, **35**, 8684.
15 X. Meng, W. Zhu, Q. Zhang, Y. Feng, W. Tan and H. Tian, *J. Phys. Chem. B*, 2008, **112**, 15636.
16 V. Barachevsky and M. Krayushkin, *Proceedings of the 4th International Symposium on Photochromism (ISOP'04)*, Arcachon, France, 2004.
17 Y. Chen and N. Xie, *J. Mater. Chem.*, 2006, **16**, 982.
18 Z. Li, Z. Chen, S. Xu, L. Niu, Z. Zhang, F. Zhang and K. Kasatani, *Chem. Phys. Lett.*, 2007, **447**, 110.
19 J. Kühni, V. Adamo and P. Belser, *Synthesis*, 2006, **12**, 1946.
20 M. Cipolloni, F. Ortica, L. Bougdid, C. Moustrou, U. Mazzucato and G. Favaro, *J. Phys. Chem. A*, 2008, **112**, 4765.
21 W. B. McCormack, *US Pat.*, 2 663 736, 1953; W. B. McCormack, *US Pat.*, 3 663 737, 1953.
22 L. D. Quin, in *1,4-Cycloaddition Reactions*, ed. J. Hamer, Academic Press, New York, 1967, ch. 3, pp. 47–96.
23 F. G. Mann, in *The Heterocyclic Derivatives of Phosphorus Arsenic Antimony and Bismuth*, Wiley-Interscience, New York, 1970, pp. 31–50.
24 L. D. Quin and D. A. Mathews, *J. Org. Chem.*, 1964, **29**, 836.
25 L. D. Quin, J. P. Gratz and T. P. Barket, *J. Org. Chem.*, 1968, **33**, 1034.
26 D. K. Myers and L. D. Quin, *J. Org. Chem.*, 1971, **36**, 1285.
27 K. Moedritzer and R. E. Miller, *Synth. React. Inorg. Met.-Org. Chem.*, 1977, **7**, 311.
28 K. Moedritzer and R. E. Miller, *Synth. React. Inorg. Met.-Org. Chem.*, 1978, **8**, 167.
29 C. Symmes and L. D. Quin, *J. Org. Chem.*, 1976, **41**, 1548.
30 F. Mathey, J.-P. Lampin and D. Thavard, *Can. J. Chem.*, 1976, **54**, 2402.
31 E. D. Middlemas and L. D. Quin, *J. Am. Chem. Soc.*, 1980, **102**, 4838.
32 L. D. Quin, E. D. Middlemas, N. S. Rao, R. W. Miller and A. T. McPhail, *J. Am. Chem. Soc.*, 1982, **104**, 1893.
33 Z. Osawa, K. Kobayashi and E. Kayano, *Polym. Degrad. Stab.*, 1985, **11**, 63.
34 K. Moedritzer, *Synth. React. Inorg. Met.-Org. Chem.*, 1975, **5**, 299.
35 W. H. Atwell and D. R. Weyenberg, *J. Am. Chem. Soc.*, 1968, **90**, 3438.
36 P. P. Garpar, in *Reactive Intermediates*, ed. M. Jr. Jones and R. A. Moss, John Wiley & Sons, New York, 1985, vol. 3, pp. 333–427.
37 P. P. Gaspar and R. West, in *The Chemistry of Organic Silicon Compounds*, ed. Z. Rappoport and Y. Apeloig, John Wiley & Sons, New York, 1998, vol. 2, pp. 2463–2568.
38 R. Maruca, *J. Org. Chem.*, 1971, **36**, 1626.
39 T. J. Barton and J. A. Kilgour, *J. Am. Chem. Soc.*, 1974, **96**, 7150.
40 T. J. Barton and J. A. Kilgour, *J. Am. Chem. Soc.*, 1976, **98**, 7746.
41 H. Appler and W. P. Neumann, *J. Organomet. Chem.*, 1986, **314**, 261.
42 J. A. Hawari and D. Griller, *Organometallics*, 1984, **3**, 1123.
43 Y. S. Cho, S.-H. Kang, J. S. Han, B. R. Yoo and I. N. Jung, *J. Am. Chem. Soc.*, 2001, **123**, 5584.
44 S.-H. Kang, J. S. Han, M. E. Lee, B. R. Yoo and I. N. Jung, *Organometallics*, 2003, **22**, 2551.
45 K. Tamao, S. Kodama, I. Nakajima, M. Kumada, A. Minato and K. Suzuki, *Tetrahedron*, 1982, **38**, 3347.
46 X. Li and H. Tian, *Tetrahedron Lett.*, 2005, **46**, 5409.
47 B. C. Fulcher, M. L. Hunter and M. E. Welker, *Synth. Commun.*, 1993, **23**, 217.
48 J. Böhmer and R. Grigg, *Tetrahedron*, 1999, **55**, 13463.
49 T.-A. Niemi, P. L. Coe and S. J. Till, *J. Chem. Soc., Perkin Trans. 1*, 2000, 1519.
50 J. Kiji, T. Okano, E. Fujii and J. Tsuji, *Synthesis*, 1997, 869.
51 A. W. Frank, *J. Org. Chem.*, 1961, **26**, 850.
52 C.-Y. Liu, J.-L. Chen, C.-C. Shiue and K.-T. Liu, *J. Chromatogr., A*, 1999, **862**, 65.
53 T. Hiyama, N. Wakasa, T. Ueda and T. Kusumoto, *Bull. Chem. Soc. Jpn.*, 1990, **63**, 640.
54 R. M. Roberts and M. B. Abdel-Baset, *J. Org. Chem.*, 1976, **41**, 1698.
55 A. Brikh and C. Morin, *J. Organomet. Chem.*, 1999, **581**, 82.
56 Y. Li, J. Ding, M. Day, Y. Tao, J. Lu and M. D'iorio, *Chem. Mater.*, 2003, **15**, 4936.
57 A. Bouillon, J.-C. Lancelot, V. Collot, P. R. Bovy and S. Rault, *Tetrahedron*, 2002, **58**, 2885.