Synthesis of Silole Skeletons via Metathesis Reactions

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Abstract: Silole skeletons are constructed by ring-closing olefin metathesis of silicon-tethered dienes and trienes. A silicon-tethered enyne is also converted to a 2-alkenyl-1-silaindene via ruthenium-catalyzed ring-closing enyne metathesis.

Key words: metathesis, silole, ruthenium, molybdenum, ring closure

The ring-closing metathesis (RCM) reaction has emerged as one of the most powerful methods for the construction of unsaturated carbo- and heterocyclic frameworks.¹ Whereas the RCM has been exploited in a number of natural product syntheses,² its applicability to the synthesis of π -conjugated functional materials remains to be explored. The potential of silole (silacyclopentadiene) derivatives³ as electron-transporting materials in OLEDs⁴ prompted us to develop a series of transition-metal-catalyzed reactions constructing silole skeletons.⁵ Herein, we report a new synthetic approach to silole derivatives, in which the silole C2–C3 double bond is created by RCM.⁶

The RCM reaction of dimethyl(alkenyl)(2-alkenylphenyl)silanes 1⁷ with several substitution patterns was examined (Table 1).^{8,9} Initially, the three conventional metathesis catalysts, i.e., the first-generation Grubbs catalyst (**Ru-I**), the second-generation Grubbs catalyst (**Ru-II**), and Schrock catalyst (**Mo**, Figure 1), were compared in the reactions of **1a** and **1b** having a phenyl group and a 3-methoxyphenyl group, respectively, as the substituent **R**.



Figure 1 Metathesis catalysts

The RCM of **1a** in toluene took place at 80 °C in the presence of **Ru-I**, giving 2-phenyl-1-silaindene **2a** in 17% yield (entry 1). The efficiency was significantly improved

SYNLETT 2008, No. 4, pp 0561–0564 Advanced online publication: 12.02.2008 DOI: 10.1055/s-2008-1032096; Art ID: U10707ST © Georg Thieme Verlag Stuttgart · New York by the use of **Ru-II**, which afforded **2a** quantitatively. When **Mo** was used as the catalyst, the RCM occurred at room temperature, giving **2a** in 89% yield. Interestingly, a different catalyst profile was observed with 3-methoxyphenyl derivative **1b**: Whereas similar results were obtained with the ruthenium complexes **Ru-I** and **Ru-II**, the more oxophilic molybdenum catalyst **Mo** failed to promote the RCM, possibly due to the coordination of the ether oxygen (entry 2).

In addition to the 2-aryl-1-silaindenes **2a** and **2b**, 2-methyl-1-silaindene **2c** was obtained in good yield from isopropenyl(2-vinylphenyl)silane **1c** (entry 3). The reaction producing 3-methyl-1-silaindene **2d** was rather sluggish with both **Ru-II** and **Mo** (entry 4). In the case of R = R' = H, unsubstituted 1-silaindene **2e** was produced in 89% with **Mo**, whereas the ruthenium catalyst **Ru-II** gave poor results (entry 5).¹⁰ The RCM of **1f** forming a tetrasubstituted olefin occurred only with the ruthenium complex, albeit in low yield (entry 6).

Thus, the RCM approach proved to function well for the synthesis of 2-substituted 1-silaindenes. Next, other sila-



Entry	Siladiene			2	Yield (%) ^b		
	1	R	R′		Ru-I	Ru-II	Мо
1	1 a	Ph	Н	2a	(17)	Quant.	89
2	1b	3-MeOC ₆ H ₄	Н	2b	(15)	96	0^{c}
3	1c	Me	Н	2c	d	91	82
4	1d	Н	Me	2d	_d	(16)	(26) ^e
5	1e	Н	Н	2e	_d	(14)	(89)
6	1f	Me	Me	2f	d	(14)	0^{c}

^a Conditions using **Ru-I**: 80 °C, 20–38 h. Conditions using **Ru-II**: 80 °C, 2–24 h. Conditions using **Mo**: r.t., 2–20 h.

^b Isolated yields by preparative TLC. Yields in parentheses refer to NMR yields.

° Conditions: 80 °C, 2-5 h.

^d Not examined.

^e Conditions: 50 °C, 4 h.

dienes 1 having various bridging groups (X) and substituents (R) were subjected to the RCM reaction using Ru-II as the catalyst of choice, and the results are summarized in Table 2. 1-Silaindenes 2g and 2h, having 4-fluorophenyl and 2-naphthyl groups at the 2-position, were obtained in excellent yields from the corresponding siladienes 1g and 1h, respectively (entries 1 and 2). Diethylsilylene and methylphenylsilylene tethers were tolerated, but required higher catalyst loading to attain good yields (entries 3 and 4). Germadiene 1k of analogous structure also underwent a RCM reaction to afford 2-germaindene 2k in high yield (entry 5). The regioisomers of methylenedioxy-substituted substrates exhibited significantly different reactivity (entries 6 and 7): Whereas 4,5-methylenedioxy derivative **11** reacted in excellent yield, the same functionality at the 3,4-positions markedly retarded the reaction.

Table 2 Synthesis of 1-Silaindenes 2 by RCM of 1 Using Ru-II^a





^b Isolated yields. Yields in parentheses refer to NMR yields.

[°] Results with 5 mol% **Mo** in toluene at r.t. for 4 h.

^d Additional catalyst (5 mol%) was added after 2 h.

^e Conditions: 110 °C, 25 h.

The RCM occurred as well when the *o*-phenylene tether of **1** was replaced by a *cis*-1,2-vinylene tether, as exemplified in Scheme 1. 2,3,5-Trisubstituted siloles **4a** and **4b** were obtained from the corresponding silatrienes **3** (Scheme 1).¹¹

A ring-closing enyne metathesis reaction¹² provides an alternative viable synthetic route to silicon-containing cyclic skeletons. The **Ru-II**-catalyzed reaction of enyne **5** in



Scheme 2 Enyne RCM

which a dimethylsilylene tether connects *o*-styryl and pent-1-ynyl groups resulted in ring closure but in both *exo* and *endo* modes¹³ to afford a 1:1 mixture of 1-silaindene **6** and 1,2-dihydro-1-silanaphthalene **7** (Scheme 2).¹⁴

The photophysical properties of selected products are listed in Table 3. For silaindenes, fluorescence maxima at 387–418 nm were observed upon irradiation at 250 nm in hexane. Considerably high fluorescence quantum efficiency (Φ_F) was observed for 2-naphthylsilaindene **2h**. Silole **4b** had longer absorption and fluorescence maxima with a larger Stokes shift in comparison to the silaindenes.

Table 3 Photophysical Properties of Products

Product	UV/vis ^a	UV/vis ^a		Fluorescence ^b		
	λ_{abs}	log ε	λ_{em}	Φ_{F}		
2a	333	4.92	387	0.83		
2h	340	4.81	396	0.96		
21	354	4.89	418	0.75		
4b	389	4.91	474	0.33		

^a Measured in CHCl₃.

^b Meaured in hexane. Determined with reference to quinine sulfate in 0.1 N H₂SO₄ and anthracene in EtOH (excited at 250 nm).

In summary, the reaction described herein provides a unique method to prepare fused and densely substituted silole compounds, some of which, like **4a** and **4b**, are difficult to synthesize using current synthetic methods.¹⁵ This route would therefore be of significant utility in the fields of organic photonics and electronics.

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(7) Preparation of Siladienes 1 Dimethyl(1-phenylvinyl)(2-vinylphenyl)silane (1a) To a solution of chlorodimethyl(2-vinylphenyl)silane (2.0 g, 10.2 mmol) in THF (10 mL) was added a solution of (1phenylvinyl)magnesium bromide in THF, which was prepared from α -bromostyrene (5.0 g, 27.3 mmol) and Mg (0.68 g, 28 mmol) in THF (20 mL) at r.t. for 3 h, at 0 °C. After the mixture was stirred at r.t. for 10 h, the volatile materials were removed under reduced pressure. The residue was quenched by sat. NH₄Cl aq solution, and extracted with hexane. The extract was dried over MgSO4 and concentrated. The residue was purified by column chromatography on silica gel(hexane). Further purification by gel-permeation chromatography (GPC) gave 1a (500 mg, 19%): ¹H NMR (300 MHz, CDCl₃): $\delta = 0.45$ (s, 6 H), 5.22 (dd, *J* = 11.0, 1.3 Hz, 1 H), 5.61 (dd, *J* = 17.4, 1.3 Hz, 1 H), 5.69 (d, J = 2.9 Hz, 1 H), 6.01 (d, J = 2.9, 1 H), 7.07–7.29 (m, 7 H), 7.35–7.41 (m, 1 H), 7.54–7.59 (m, 2 H). ¹³C NMR $(75 \text{ MHz}, \text{CDCl}_3): \delta = -1.0, 114.9, 125.2, 126.4, 126.8,$ 126.9, 128.1, 129.0, 129,6, 135.1, 136.0, 138.0, 134.9, 144.0, 151.5. HRMS (EI): m/z [M]⁺ calcd for C₁₈H₂₀Si:

264.1334; found: 264.1335.

Isopropenyldimethyl(2-vinylphenyl)silane (1c) ¹H NMR (300 MHz, CDCl₃): $\delta = 0.40$ (s, 6 H), 1.80 (t, *J* = 1.4 Hz, 3 H), 5.22 (dd, *J* = 10.8, 1.2 Hz, 1 H), 5.36 (q, *J* = 0.9 Hz, 1 H), 5.64 (dd, *J* = 17.3, 1.2 Hz, 1 H), 5.69 (sext, J = 1.7 Hz, 1 H), 7.04 (dd, J = 17.3, 10.8 Hz, 1 H), 7.25 (dt, *J* = 1.3, 7.3 Hz, 1 H), 7.37 (dt, *J* = 1.5, 7.5 Hz, 1 H), 7.50 (dd, J = 7.4, 1.4 Hz, 1 H), 7.56 (d, J = 7.5 Hz, 1 H). ¹³C NMR (75 MHz, CDCl₃): δ = -2.1, 22.6, 114.7, 125.0, 126.5, 126.9, 129.5, 135.0, 135.7, 138.0, 144.1, 146.6. HRMS (EI): m/z $[M]^+$ calcd for $C_{13}H_{18}Si: 202.1178$; found: 202.1173. Dimethyl(1-phenylvinyl)(2-vinylphenyl)germane (1k) ¹H NMR (300 MHz, CDCl₃): $\delta = 0.57$ (s, 6 H), 5.22 (dd, J = 10.5, 1.5 Hz, 1 H), 5.55 (d, J = 2.1 Hz, 1 H), 5.63 (dd, J = 17.4, 1.2 Hz, 1 H), 6.03 (d, J = 2.1 Hz, 1 H), 6.98 (dd, J = 17.4, 11.1 Hz, 1 H), 7.15–7.28 (m, 6 H), 7.32–7.38 (m, 1 H), 7.49–7.53 (m, 1 H), 7.56–7.60 (m, 1 H). ¹³C NMR (75 MHz, CDCl₃): $\delta = -1.1$, 115.0, 125.1, 126.0, 126.6 [overlapping], 127.1, 128.2, 129.1, 134.3, 137.8, 139.0, 143.2, 143.5, 152.2. HRMS (EI): m/z [M]⁺ calcd for C₁₈H₂₀Ge: 310.0777; found: 310.0786.

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- (9) General Procedure for Ring-Closing Metathesis 1,1-Dimethyl-2-phenyl-1-silaindene (2a)¹ To Schrock catalyst (11.5 mg, 0.015 mmol) was added a solution of **1a** (76.45 mg, 0.289 mmol) in toluene (5 mL), and the mixture was stirred at r.t. for 2 h. The reaction mixture was taken up with hexane and passed through a pad of Florisil®. Removal of volatile materials afforded 2a (61.4 mg, 0.257 mmol, 89%): ¹H NMR (300 MHz, CDCl₃): $\delta = 0.48$ (s, 6 H), 7.20–7.40 (m, 6 H), 7.49–7.56 (m, 4 H). ¹³C NMR (75 MHz, CDCl₃): $\delta = -3.1$, 124.3, 126.4, 126.6, 127.0, 128.7, 130.0, 131.7, 138.2, 139.0, 141.1, 145.3, 148.8. ²⁹Si NMR (79 MHz, CDCl₃): $\delta = -15.9$. HRMS (EI): m/z [M]⁺ calcd for C₁₆H₁₆Si: 236.1021; found: 236.1019. 2-(3-Methoxyphenyl)-1,1-dimethyl-1-silaindene (2b) To Grubbs second-generation catalyst (8.7 mg, 0.010 mmol) was added a solution of 1b (58.62 mg, 0.199 mmol) in toluene (2 mL), and the mixture was stirred at 80 °C for 2 h. The reaction mixture was taken up with hexane and passed through a pad of Florisil[®] (hexane–EtOAc = 10:1). After removal of volatile materials, the residue was subjected to preparative thin-layer chromatography to give 2b (50.66 mg, 0.190 mmol, 96%): ¹H NMR (300 MHz, CDCl₃): $\delta = 0.49$ (s, 6 H), 3.87 (s, 3 H), 6.79–6.85 (m, 1 H), 7.04–7.11 (m, 2 H), 7.19-7.39 (m, 4 H), 7.53-7.57 (m, 2 H). 13C NMR (75 MHz, CDCl₃): $\delta = -3.1, 55.2, 111.9, 112.4, 119.3, 124.3, 126.7,$ 129.6, 130.0, 131.7, 138.3, 140.5, 141.5, 145.2, 148.7, 159.8. HRMS (EI): m/z [M]⁺ calcd for C₁₇H₁₈OSi: 266.1127; found: 266.1121.

1,1,2-Trimethyl-1-silaindene (2c)

¹H NMR (300 MHz, CDCl₃): $\delta = 0.28$ (s, 6 H), 2.02 (d, J = 1.5 Hz, 3 H), 6.86 (q, J = 1.5 Hz, 1 H), 7.10–7.15 (m, 2 H), 7.24–7.30 (m, 1 H), 7.46 (d, J = 6.9 Hz, 1 H). ¹³C NMR (75 MHz, CDCl₃): $\delta = -4.6$, 17.4, 122.8, 125.6, 129.7, 131.6, 138.1, 142.7, 144.6, 149.5. HRMS (EI): m/z [M]⁺ calcd for C₁₁H₁₄Si: 174.0865; found: 174.0864.

1,1,3-Trimethyl-1-silaindene (2d)

 $\label{eq:solution} \begin{array}{l} {}^{1}\text{H NMR (300 MHz, CDCl_3): } \delta = 0.29 \ (\text{s}, 6 \ \text{H}), 2.22 \ (\text{s}, 3 \ \text{H}), \\ 5.92 \ (\text{s}, 1 \ \text{H}), 7.21 \\ -7.27 \ (\text{m}, 1 \ \text{H}), 7.30 \\ -7.40 \ (\text{m}, 2 \ \text{H}), 7.51 \\ -7.55 \ (\text{m}, 1 \ \text{H}). \, \, \, ^{13}\text{C NMR} \ (75 \ \text{MHz}, \text{CDCl}_3): \\ \delta = -4.0, 19.6, \\ 121.2, 126.5, 127.8, 129.4, 131.2, 139.8, 149.9, 156.2. \, \, ^{29}\text{Si} \end{array}$

NMR (79 MHz, CDCl₃): δ = -19.4. HRMS (EI): *m*/z [M]⁺ calcd for C₁₁H₁₄Si: 174.0865; found 174.0864. **1,1-Diethyl-2-phenyl-1-silaindene (2i)** ¹H NMR (300 MHz, CDCl₃): δ = 0.85–1.15 (m, 10 H), 7.18– 7.58 (m, 10 H). ¹³C NMR (75 MHz, CDCl₃): δ = 4.3, 7.5, 124.2, 126.39, 126.45, 126.9, 128.6, 129.9, 132.3, 136.3, 139.5, 142.4, 143.7, 149.7. ²⁹Si NMR (79 MHz, CDCl₃): δ = -8.7. HRMS (EI): *m*/z [M]⁺ calcd for C₁₈H₂₀Si: 264.1334; found 264.1332. **1,1-Dimethyl-2-phenyl-1-germaindene (2k)**

¹H NMR (300 MHz, CDCl₃): $\delta = 0.67$ (s, 6 H), 7.20–7.41 (m, 6 H), 7.47–7.58 (m, 4 H). ¹³C NMR (75 MHz, CDCl₃): $\delta = -2.2$, 125.0, 126.6, 126.8, 127.1, 128.7, 129.3, 131.8, 137.8, 139.3, 140.5, 147.6, 148.0. HRMS (EI): m/z [M]⁺ calcd for C₁₆H₁₆Ge: 282.0464; found: 282.0469.

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- (11) Dimethyl(1-phenylvinyl)(2-vinylcyclopent-1-enyl)silane (3a)

A solution of (2-vinylcyclopent-1-enyl)lithium in THF, which was prepared from 1-bromo-2-vinylcyclopent-1-ene (0.69 g, 3.99 mmol) and n-BuLi in hexane (1.55 M, 2.8 mL, 4.34 mmol) in THF (10 mL) at -78 °C for 1 h, was added to a solution of chlorodimethyl(1-phenylvinyl)silane (0.697 g, 3.54 mmol) in THF (10 mL) at 0 °C. After the mixture was stirred at r.t. for 10 h, the volatile materials were removed under reduced pressure. The residue was quenched by sat. NH₄Cl aq solution, and extracted with hexane. The extract was dried over MgSO4 and concentrated. The residue was purified by column chromatography on silica gel (hexane) to afford **3a** (0.32 mg, 32%): ¹H NMR (300 MHz, CDCl₃): $\delta = 0.29$ (s, 6 H), 1.82 (quin, J = 7.5 Hz, 2 H), 2.47–2.60 (m, 4 H), 5.09 (d, J = 10.7 Hz, 1 H), 5.13 (d, J = 17.1 Hz, 1 H), 5.65 (d, *J* = 3.0 Hz, 1 H), 5.92 (d, *J* = 3.0 Hz, 1 H), 6.80 (dd, J = 17.1, 10.7 Hz, 1 H), 7.15–7.30 (m, 5 H). ¹³C NMR (75 MHz, CDCl₃): δ = -1.2, 23.6, 34.6, 39.3, 115.3, 126.6, 127.0. 128.2. 128.3, 134.3, 140.9, 144.5, 151.9, 152,7. HRMS–FAB: *m/z* calcd for C₁₇H₂₂Si [M⁺] 254.1491; found: 254.1476.

Dimethyl(1-phenylvinyl)(2-vinyl-3,4-dihydronaph-thalen-1-yl)silane (3b)

¹H NMR (300 MHz, CDCl₃): $\delta = 0.45$ (s, 6 H), 2.31–2.38 (m, 2 H), 2.58–2.65 (m, 2 H), 5.16 (d, J = 10.8 Hz, 1 H), 5.44 (d, J = 17.1 Hz, 1 H), 5.78 (d, J = 2.7 Hz, 1 H), 5.97 (d, J = 2.7 Hz, 1 H), 6.96 (dd, J = 17.1, 11.1 Hz, 1 H), 7.09–7.26 (m, 9 H). ¹³C NMR (75 MHz, CDCl₃): $\delta = 2.0$, 24.4, 28.5, 114.3, 125.6, 125.9, 126.4, 126.7, 126.8, 127.5, 128.0, 128.1, 135.7, 136.7, 138.1, 138.7, 143.9, 150.6, 153.3. HRMS (EI): m/z [M]⁺ calcd for C₂₂H₂₄Si: 316.1647; found: 316.1650.

1,1-Dimethyl-2-phenyl-1,4,5,6-tetrahydrocyclopenta[*b*]silole (4a)

¹H NMR (300 MHz, CDCl₃): $\delta = 0.37$ (s, 6 H), 2.14 (quin, J = 7.2 Hz, 2 H), 2.48–2.59 (m, 4 H), 7.12–7.43 (m, 6 H). ¹³C NMR (75 MHz, CDCl₃): $\delta = -3.7$, 27.0, 32.7, 32.8, 125.9, 126.4, 128.6, 134.9, 139.5, 142.9, 147.5, 161.4. HRMS–FAB: m/z [M]⁺ calcd for C₁₅H₁₈Si: 226.1178; found: 226.1187.

2-Phenyl-4,5-dihydronaphtho[1,2-*b*]silole (4b) ¹H NMR (300 MHz, CDCl₃): $\delta = 0.55$ (s, 6 H), 2.59 (t, *J* = 8.4 Hz, 2 H), 2.92 (t, *J* = 8.1 Hz, 2 H), 7.08–7.50 (m, 10 H). ¹³C NMR (75 MHz, CDCl₃): $\delta = -2.7$, 26.3, 28.4, 125.7, 126.1, 126.2, 126.6, 126.8, 127.86 128.7, 134.2, 134.6, 135.9, 138.7, 140.9, 144.7, 152.2. ²⁹Si NMR (79 MHz, CDCl₃): $\delta = -16.2$. HRMS (EI): *m*/*z* [M]⁺ calcd for C₂₀H₂₀Si: 288.1334; found: 288.1330.

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 - H), 7.52–7.54 (m, 1 H). ¹³C NMR (75 MHz, CDCl₃): $\delta = -2.9$, 14.0, 21.6, 35.9, 115.0, 124.2, 126.5, 129.9, 131.6, 138.3, 140.5, 146.8, 147.3, 149.0. HRMS (EI): m/z [M]⁺ calcd for C₁₅H₂₀Si: 228.1334; found: 228.1333.
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