Unexpected cross-metathesis between Si–C and Si–Si bonds

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In the presence of a palladium complex, the Si–C bond of [1]silaferrocenophane or 1-silacyclobutanes undergoes selective cross-metathesis reaction with the Si–Si bond of strained-cyclic or activated-acyclic disilanes.

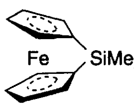
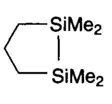
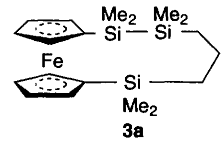
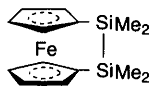
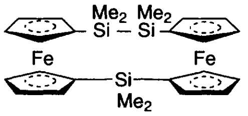
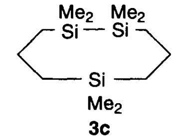
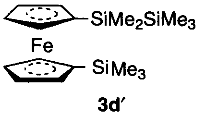
In relation to the ring-opening cyclo-oligomerization and polymerization of cyclic disilanes,[1] there is a strong renewed interest in the Si–Si bond metathesis reaction.[2] On the other hand, silacyclobutanes[3] and [1]silaferrocenophanes[4] have been found to undergo metal complex-catalysed oligomerization or polymerization, which is formally a metathesis reaction between Si–C bonds. Palladium-catalysed dimerization of silacyclopropene to 1,4-disilacyclohexadiene[5] is another example of the Si–C bond metathesis. However, selective cross-metathesis of Si–C and Si–Si bonds has never been documented. During our investigation on the reactivity of Si–C bonds of [1]silaferrocenophanes and 1-silacyclobutanes, we accidentally came across such reactions. Herein, we report the preliminary results of this unprecedented Si–C/Si–Si metathesis reaction.

In a typical experiment, a benzene (0.5 ml) solution of dimethylsilylene-bridged [1]ferrocenophane **1a** (0.2 mmol), 1,1,2,2-tetramethyl-1,2-disilacyclopentane **2a** (0.2 mmol) and [PdCl$_2$(PMe$_3$)$_2$] (0.008 mmol) was heated in a sealed NMR tube at 100 °C for 12 h (Scheme 1). ^{1}H NMR (C$_6$D$_6$) of the reaction mixture showed that the resonances for the starting materials in the Si–Me region were cleanly replaced by three new resonances (δ 0.19, 0.2, 0.30), while, in the cyclopentadienyl region, two sets of pseudo-quartets appeared in place of two triplets corresponding to **1a**. Similarly, ^{29}Si NMR of the reaction mixture showed three resonances at δ −20.90, −13.52 and −2.98, confirming the complete conversion of the starting materials and nearly quantitative formation of the codimer **3a**. The reaction mixture was subjected to preparative TLC using hexane as eluent to afford analytically pure **3a** in 94% yield (Table 1, entry 1).[†]

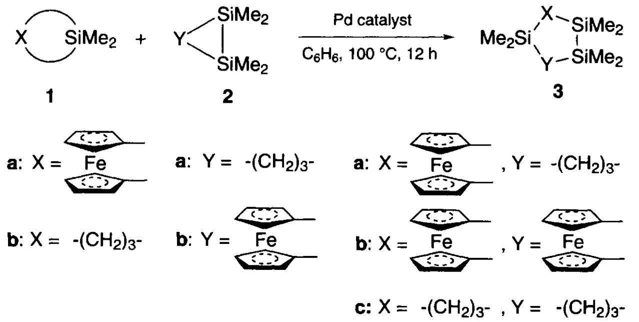
The reactions of **1a** with tetramethyldisilanylene-bridged [2]ferrocenophane **2b** and of 1,1-dimethylsilacyclobutane **1b** with **2a** proceeded similarly to give codimers **3b** and **3c**.[†] Experiments run under the same conditions as entry 2, comparison of catalytic performance in the reaction of **1a** with **2b** showed that palladium trialkylphosphine complexes such as [PdCl$_2$(PEt$_3$)$_2$], [PdCl$_2$(PBu$_3$)$_2$] and [PdCl$_2$(dbpb)] [dbpb = 1,4-bis(dibutylphosphino)butane] were found to be almost equally active; yields (^{1}H NMR) of **3b** were about 80% in all cases. However, [PdCl$_2$(PPh$_3$)$_2$] was not efficient for the codimerization reaction, the ^{1}H NMR yield of **3b** being only 38%.

Interestingly, similar Si–C/Si–Si metathesis reactions could proceed between **1a** and a linear disilane when the disilane was activated. Thus, the reaction of **1a** with 1,2-difluorotetramethyldisilane **2c** under identical conditions formed 1-(2-fluoro-1,1,2,2-tetramethyldisilanyl)-1′-fluorodimethylsilylferrocene **3d**[†] as major product (*ca.* 70% by NMR) (Scheme 2). Treatment of the resulting mixture with MeLi followed by preparative TLC (hexane as eluent) afforded an analytically pure methylated product **3d′** in 51% isolated yield (entry 4), along with trimethylsilylferrocene (22%) that came from the reaction of unreacted **1a** and MeLi.[6]

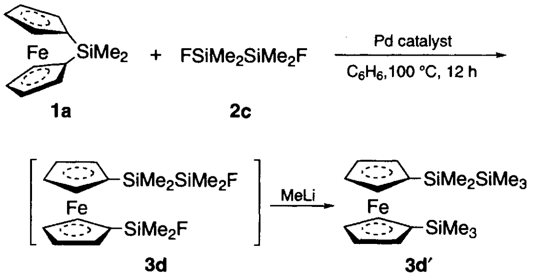
Table 1 Palladium-catalysed metathesis of [1]silaferrocenophane **1a** or 1-silacyclobutane **1b** with disilanes **2**[a]

Entry	1	2	Product 3	Yield(%)[b]
1	 **1a**	 **2a**	 **3a**	94 (98)
2	**1a**	 **2b**	 **3b**	65 (80)
3	 **1b**	**2a**	 **3c**	70 (78)
4	**1a**	FMe$_2$Si—SiMe$_2$F **2c**	 **3d′**	51

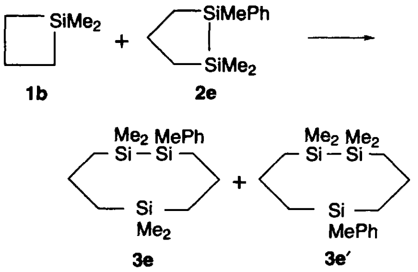
[a] **1** 0.2 mmol; **2**, 0.2 mmol; [PdCl$_2$(PMe$_3$)$_2$], 0.008 mmol; 100 °C, 12 h. [b] Isolated yields based on the charged amount of **1** or **2**. NMR yields are given in parentheses. [c] Product isolated by TLC after treatment of the reaction mixture with MeLi.



Scheme 1



Scheme 2



Scheme 3 Combined NMR yield = 60%, **3e**/**3e′** ≈ 5

As the results indicate, the reaction of **1a** or **1b** with a disilane is highly dependent on the environment around the Si–Si bond. In addition, the reaction of **1a** or **1b** with 1,1,2,2-tetramethyl-1,2-disilacyclohexane did not produce any codimer.‡

It is interesting that **1b** and **2a** are known to undergo homodimerization reaction in the presence of transition-metal complexes.[1d,1e,2a,3] However, barring the reaction of **1b** with **2a** (entry 3, in which < 2% of the homodimer of **2a** was detected), the dimers of **1** or **2** were not observed in an appreciable quantity in any of the above reactions.§ Thus, it is a selective cross-metathesis reaction of Si–C/Si–Si bonds. The following reaction stands as confirmatory evidence for the Si–C/Si–Si metathesis reaction. The treatment of **1a** with 1-phenyl-1,2,2-trimethyl-1,2-disilacyclopentane **2e** produced two expected isomeric products, **3e** and **3e′**† (60% in total, **3e**/**3e′** ≈ 5), under similar conditions (Scheme 3). Thus, a possible involvement of a Si–C bond in the disilane, *i.e.* a Si– C/Si–C cross-metathesis, can be ruled out.

The mechanism of the selective Si–C/Si–Si metathesis is ambiguous at the moment. One of possible mechanisms may involve the oxidative addition of the Si–C bond of **1** with the palladium centre. Although we have been unable to confirm such oxidative addition between **1a** and Pd^0 species, **1b** does react with Pt^0[3d] or Pd^0[7] species. In addition, the Si–C bond of **1a** also reacted at 60–80 °C with $[Pt(PEt_3)_3]$ to give the corresponding adduct nearly quantitatively.[8,9] On the other hand, the oxidative addition of **2b** with $[Pt(PEt_3)_3]$, although it proceeded at 80 °C, was much slower.[10] Accordingly, a mechanism initiated by the oxidative addition of the Si–C bond of **1a** or **1b** appears likely. However, our previous observation[11] that **2c** reacted nearly instantaneously with $[Pt(PEt_3)_3]$ at room temperature also suggests the possibility of another mechanism initiated by the oxidative addition of the Si–Si bond. Although further details still remain to be clarified, we believe either of these two options is possible, depending on the reactivity of Si–C and Si–Si bonds in the starting materials.

In conclusion, [1]silaferrocenophane and 1-silacyclobutane underwent selective Si–C/Si–Si bond cross-metathesis reactions with strained-cyclic or activated-acyclic disilanes. The reaction provides new insights into differentiation of Si–C and Si–Si bonds by transition-metal complexes and offers new silylferrocene derivatives, which may be useful to synthesize functional materials.[12]

Footnotes

† *Work-up procedure for* **3a**, **c**, **e**: the reaction mixture was subjected to preparative TLC using hexanes as eluent. For **3b**: the reaction mixture was filtered through florisil, concentrated and washed with small amounts (*ca.* 1 ml) of cold hexane. For **3d′**: the reaction mixture was treated at room temp. with a 4-fold excess of MeLi (1.4 mol dm^{-3} in Et_2O), stirred for 30 min and quenched with propan-2-ol. The solution was concentrated and the product was separated by preparative TLC using hexanes as eluent.

Selected spectral and analytical data: (NMR, C_6D_6; ^1H NMR, 300 Mz; ^{29}Si NMR, 59.6 Mz; *J*/Hz). For **3a**: orange–red viscous liquid. ^1H NMR δ 0.19 (s, 6 H, $SiMe_2$), 0.20 (s, 6 H, $SiMe_2$), 0.30 (s, 6 H, $SiMe_2$), 0.89–0.97 (m, 4 H, $SiCH_2$), 1.96–2.06 (m, 2 H, $CH_2CH_2CH_2$), 4.08 (pseudo q, 4 H, C_5H_4), 4.18 (pseudo q, 4 H, C_5H_4). ^{29}Si NMR δ −20.89, −13.52, −2.98. For **3b**: orange–red crystals. mp 168–170 °C. ^1H NMR δ 0.37 (s, 12 H, $SiMe_2$–$SiMe_2$), 0.38 (s, 6 H, $C_5H_4SiMe_2C_5H_4$), 4.24 (t, *J* 1.65, 4 H, C_5H_4), 4.26 (*t*, *J* 1.65, 4 H, C_5H_4), 4.30 (t, *J* 1.65, 4 H, C_5H_4), 4.36 (t, *J* 1.65, 4 H, C_5H_4). ^{29}Si NMR δ −18.31 (2Si, Si–Si), −5.47 (1Si, $C_5H_4SiC_5H_4$). For **3c**: colourless viscous liquid. ^1H NMR δ 0.01 (s, 6H, $CH_2SiMe_2CH_2$), 0.09 (s 12 H, $SiMe_2SiMe_2$), 0.66–0.70 (m, 4 H, $SiCH_2$), 0.82–0.87 (m 4 H, $SiCH_2$), 1.70–1.77 (m, 4 H, $CH_2CH_2CH_2$). ^{29}Si NMR δ −17.99 (2Si, $SiMe_2SiMe_2$), 3.68 (1Si, $CH_2SiMe_2CH_2$). For **3d**: ^{29}Si NMR δ −24.29 (d, $^2J_{SiF}$ 26.7 Hz, $C_5H_4SiMe_2SiMe_2F$), 23.5 (d, $^1J_{SiF}$ 275.95, $SiMe_2F$), 33.05 (d, $^1J_{SiF}$ 308.55, $SiMe_2F$). For **3e**: colourless viscous liquid. ^{29}Si NMR δ −19.87, −17.86, 3.68. For **3e′**: colourless viscous liquid. ^{29}Si NMR δ −21.36 (2Si, Si–Si), 1.95 (1Si, SiMePh).

‡ A small amount of homodimer of **1b** was detected by GCMS.

§ In the reactions of **1a**, a small amount of a polymer of **1a** (< 5%) was observed. It is noted that the ROP of **1a** proceeds at 120 °C (ref. 13).

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