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Studies on the Pd-Catalyzed Dimerization of Silacyclobutanes

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Abstract

Dimerization of silacyclobutanes has been achieved under palladium catalysis at room temperature. A previous report described the requirement for high temperature and a stoichiometric amount of palladium complex to effect this process.

Introduction

Silicon is the second most abundant element on Earth after oxygen however its use in synthetic chemistry is limited, especially compared to its group neighbor carbon.[1] This is surprising considering silicon's abundance, sustainability and known non-toxicity to humans. Importantly, exchanging carbon atoms for silicon atoms in small molecules can have a profound effect on the properties of the compound. This has been demonstrated in silicon-analogs of drug molecules such as sila-haloperidol.[2] In addition, dibenzosiloles have been reported to have unique optoelectronic properties and have found use as light-emitting diodes,[3] thin-film transistors,[4] solar cells[5] and detectors for explosives.[6] These silicon molecules have generally been shown to be superior to their carbon analogues.

There has been significant interest in the synthesis and reactions of cyclic silicon compounds.[7] In particular, silacyclobutanes have been polymerized by a range of late transition metals[8] and been shown to be useful in Pd-catalyzed ring expansion processes.[9] Interestingly, the work on the ring expansions has shown that oxidative addition to silacyclobutanes by Pd(0) complexes is not facile and that generally ring opening occurs by Pd(II). However, Tanaka and co-workers have demonstrated that Pd(η^2-PhCH=CH$_2$)(dmpe) reacts with 1,1-dimethyl- and 1,1-diphenylsilacyclobutane **1** in quantitative yield at room temperature to form the five-membered palladacycle **2** (Scheme 1).[10] Upon heating the 1,1-diphenyl palladacycle **2b** at 100 °C with an excess of 1,1-dimethylsilacyclobutane **1a** for 30 hours an eight-membered ring **3ab** was obtained in 44% yield. In this Communication, we describe our findings on the Pd-catalyzed version of this process which occurs at room temperature.
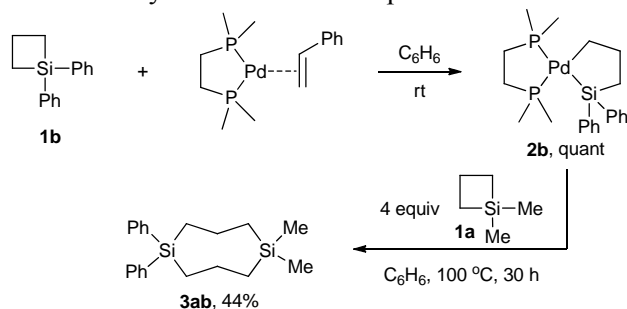
Scheme 1 Stoichiometric Pd-mediated pseudo-dimerization of silacyclobutanes

Results and Discussion

In an effort to develop a catalytic version of this process we stirred silacyclobutane**1a** in toluene at room temperature in the presence of 5 mol% Pd(OAc)$_2$, and we were delighted to find a small amount of dimer **3aa** was formed by ^{1}H NMR analysis. Unfortunately, a pure sample of **3aa** could not be obtained (Table 1, entry 1). A variety of Pd(0) and Pd(II) salts were investigated to determine whether they would catalyze this process (entries 2-8), however all salts led to unreacted **1a** being recovered apart from Pd(MeCN)$_4$(BF$_4$)$_2$ (entry 8). The effect of temperature on the reaction outcome was investigated and the yield was increased to 35% upon heating to 40 ^{o}C (entry 9), however a further rise to 60 ^{o}C did not result in any additional increase in yield (entry 10). Increasing the amount of catalyst to 10 mol% resulted in 39% yield of isolated compound at room temperature just 10 minutes (entry 11). However, further increases in catalyst loading or increasing the reaction temperature did not lead to any additional yield augmentation. Indeed, complete consumption of the silacyclobutane**1a** was observed, but no other products could be isolated by chromatography. 1,4-Dioxane, acetonitrile and benzene were shown not to be suitable solvents for this process and the addition of 5 mol% CuCl or water inhibited the reaction completely (entries 12-16). Heating the reaction mixtures containing any of the other Pd-species did not lead to dimerization.

Table 1 Investigation of catalytic conditions for the dimerization of **1a**

Entry	Catalyst	Solvent	Temp (^{o}C)	Yield (%)
1	Pd(OAc)$_2$	toluene	r.t.	<5
2	Pd(PPh$_3$)$_4$	toluene	r.t.	0
3	Pd(dba).CHCl$_3$	toluene	r.t.	0
4	Pd/C	toluene	r.t.	0
5	PdCl$_2$	toluene	r.t.	0
6	Pd(OCOCF$_3$)$_2$	toluene	r.t.	0
7	PEPPSI-IPr	toluene	r.t.	0
8	Pd(MeCN)$_4$(BF$_4$)$_2$	toluene	r.t.	14
9	Pd(MeCN)$_4$(BF$_4$)$_2$	toluene	40	35
10	Pd(MeCN)$_4$(BF$_4$)$_2$	toluene	60	34
11	Pd(MeCN)$_4$(BF$_4$)$_2$	toluene	r.t.	39[a]
12	Pd(MeCN)$_4$(BF$_4$)$_2$	1,4-dioxane	r.t.	0
13	Pd(MeCN)$_4$(BF$_4$)$_2$	MeCN	r.t.	0
14	Pd(MeCN)$_4$(BF$_4$)$_2$	benzene	r.t.	0
15	Pd(MeCN)$_4$(BF$_4$)$_2$/CuCl	toluene	r.t.	0
16	Pd(MeCN)$_4$(BF$_4$)$_2$	toluene	r.t.	0[b]

[a] 10 mol% catalyst used. [b] 1 equiv of H$_2$O added to reaction mixture. PEPPSI-IPr is [1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene](3-chloropyridyl)palladium(II) dichloride.

When these catalytic reaction conditions were applied to silacyclobutanes **1b-d** no dimerization occurred and they were recovered unconverted (Scheme 2). This suggests that steric considerations are very important for the initial oxidative addition step to the silacyclobutane.
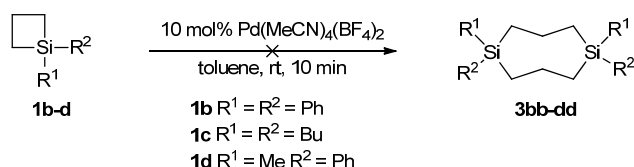
Scheme 2 Pd-catalyzed dimerization of silacyclobutanes **1b-d** does not occur.

In order to investigate any differences between the reactivity of the different palladium species present during the course of the reaction, a 1:1 mixture of silacyclobutanes **1a** and **1b** was prepared and subjected to the reaction conditions. Analysis by NMR showed that a ~1:1 mixture of the two products **3aa** and **3ab** were formed. Repeating the reaction with a 1:2 ratio of **1a** and **1b** led to the

formation of a ~1:2 ratio of **3aa** and **3ab**. These results indicate that although the initial oxidative addition only occurs with **1a**, the subsequent step in the reaction mechanism is of similar rate with **1a** and **1b**.
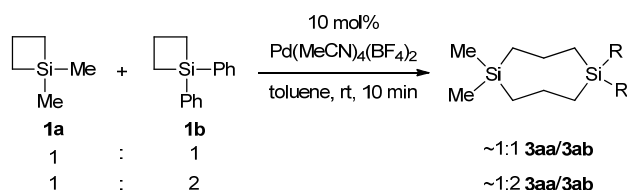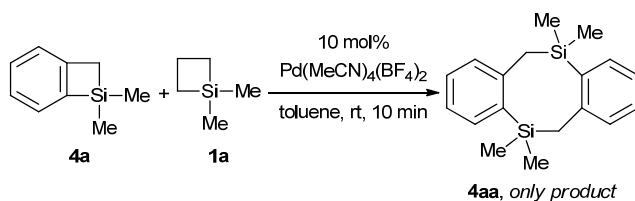

Scheme 3 Competition reaction showing relative reactivities of **1a** and **1b**.

1,1-Dimethylbenzosiletane **4a** was prepared and subjected to the dimerization reaction conditions and the desired product was obtained in 31% yield (Scheme 4). In analogy to **1b**, the diphenyl analog of **4a** did not undergo the dimerization process either.
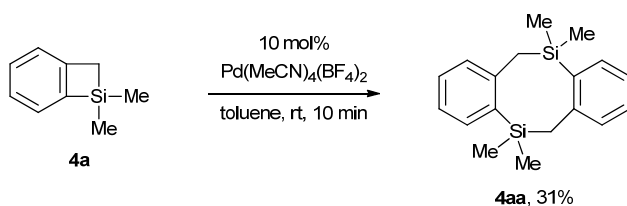
Scheme 4 Pd-catalyzed dimerization of **4a**.

It was anticipated that compound **4a** would be more reactive than **1a** due to the activation of the C-Si bond by the aromatic ring. In order to probe the reactivity difference, should there be any, a 1:1 mixture of **1a** and **4a** was subjected to the reaction conditions (Scheme 5). In the event, only product **4aa** was observed in the crude reaction mixture suggesting that **4a** reacts faster than **1a** in both stages of the dimerization process.

Scheme 5 Competition reaction showing relative reactivities of **1a** and **4a**.

The dimerization of **1a** was attempted using the standard reaction conditions but in the presence of one equivalent of galvinoxyl. No effect on the rate or outcome of the reaction was evident from this experiment suggesting that this is not a radical process. A second experiment was conducted by added one equivalent of mercury to the reaction mixture and, in this case, complete inhibition of the dimerization was observed. Manners and co-workers have studied the ring-opening polymerization of silicon-bridged [1]ferrocenophanes and observed the dimerization of these compounds during their study.[11] In analogy with their work, this mercury inhibition suggests that a heterogeneous catalytic mechanism is operating in the dimerization of silacyclobutanes. The very labile ligands required on palladium for this dimerization process to occur is another indication for palladium colloid formation.

Based on these observations, we propose that the palladium salt Pd(MeCN)$_4$(BF$_4$)$_2$ forms palladium colloids under the reaction conditions. These undergo oxidative addition to silacyclobutane **1a** or **4a** and then combine with another molecule of silacyclobutane followed by reductive elimination to furnish the dimer.

Experimental

General

^{1}H NMR spectra were recorded at 400 MHz in CDCl$_3$ unless otherwise stated. Chemical shifts are reported in ppm from tetramethylsilane with the solvent resonance as the internal standard (CDCl$_3$: 7.26 ppm). Data are reported as follows: chemical shift, integration, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, br = broad, m = multiplet), and coupling constants (Hz). ^{13}C NMR were recorded at 100 MHz in CDCl$_3$ unless otherwise stated with complete proton decoupling. Chemical shifts are reported in ppm from tetramethylsilane with the solvent as the internal standard (CDCl$_3$: 77.4 ppm). ^{29}Si NMR spectra were recorded at 99 MHz in CDCl$_3$. Mass spectrometry (m/z) was performed in EI or APCI mode, with only molecular ions being reported. Infrared (IR) spectra ν_{max} are reported in cm^{-1}. Bands are characterized as broad (br), strong (s), medium (m) and weak (w). All purchased reagents were used as received without further purification. Dimethyl silacyclobutane **1a** is commercially available. The other silacyclobutanes **1b**,[12] **1c**,[13] **1d**[14] and **4a**[15] were prepared by literature methods and the analytical data matched the literature values. The 1,5-disilocanes **3aa**,[8d] **3ab**[8d] and **4aa**[16] are known compounds and the analytical data matched the literature values.

Synthesis of 1,1,5,5-tetramethyl-1,5-disilocane **3aa**.[8d]
A mixture of 1,1-dimethylsilacyclobutane **1a** (50 mg, 0.5 mmol) and tetrakis(acetonitrile) palladium(II) tetrafluoroborate (22 mg, 0.05 mmol) in toluene (2 mL) was stirred for ten minutes at room temperature. The mixture was filtered through Celite and the filter pad washed with ethyl acetate (10 mL). Concentration under vacuum afforded 1,1,5,5-tetramethyl-1,5-disilocane **3aa** as a colourless oil (19.5 mg, 39%). IR (neat): 1220 (m), 1359 (m), 1708 (s). ^{1}H NMR: δ-0.05 (12H, s), 0.74 (8H, t, *J* = 6.9 Hz), 1.77 (4H, q, *J* = 6.9 Hz). ^{13}C NMR: δ -2.1 (4C), 18.3 (4C), 18.7 (2C). ^{29}Si NMR: δ 2.38. MS (EI): [M-CH$_3$]$^+$ 185.1.

Competition reaction between **1a** and **1b**: synthesis of 1,1-dimethyl-5,5-diphenyl-1,5-disilocane **3ab**.[8d]
A mixture of 1,1-diphenylsilacyclobutane **1b** (50 mg, 0.2 mmol, 1 equiv), 1,1-dimethylsilacyclobutane **1a** (28 mg, 0.2 mmol, 1 equiv), and tetrakis(acetonitrile)palladium(II) tetrafluoroborate (8 mg, 0.02 mmol) in toluene (3 mL) was stirred overnight at room temperature. The mixture was filtered through Celite and the filter pad washed with ethyl acetate (10 mL). Concentration under vacuum afforded a circa 1:1 mixture of **3aa** and **3ab** as a colorless oil. Separation of these compounds by flash chromatography was not successful. NMR data for **3ab**: ^{1}H NMR: δ 0.01 (6H, s), 0.85 (4H, t, *J* = 6.8 Hz), 1.44 (4H, t, *J* = 6.8 Hz), 1.94 (4H, q, *J* = 6.8 Hz), 7.27-7.63 (10H, m). ^{13}C NMR: δ -2.5 (2C), 14.7 (2C), 18.1 (2C), 18.3 (2C), 127.8 (4C), 128.9 (4C), 134.3 (2C), 137.5 (2C). ^{29}Si NMR: δ -7.66, 2.72.

Synthesis of 5,5,11,11-tetramethyl-5,6,11,12-tetrahydrodibenzo[b,f][1,5]disilocine **4aa**.[16]
7,7-Dimethyl-7-silabicyclo[4.2.0]octa-1(6),2,4-triene (100 mg, 0.67 mmol, 1 equiv) (**4a**) was dissolved in toluene (2 mL). Then, tetrakis(acetonitrile)palladium(II) tetrafluoroborate (29 mg, 0.067 mmol) was added and the mixture was stirred at room temperature for 10 minutes. The mixture was filtered through Celite and the filter pad washed with ethyl acetate (10 mL). The filtrate was concentrated under vacuum and purified by flash chromatography (petroleum ether 40-60 on silica) to give 5,5,11,11-tetramethyl-5,6,11,12-tetrahydrodibenzo[b,f][1,5]disilocine **4aa** as a colourless oil (0.077 g, 31%). IR (neat): 724 (s), 799 (s), 1430 (m), 2946 (w). ^{1}H NMR: δ 0.33 (6H, s), 0.38 (6H, s), 2.33 (2H, d, *J* = 13.5 Hz), 2.77 (2H, d, *J* = 13.5 Hz), 6.90 (2H, td, *J* = 7.4, 1.0 Hz), 6.95 (2H, d, *J* = 7.6 Hz), 7.10-7.16 (4H, m). ^{13}C NMR: δ -3.2, -1.1, 29.4 (4C), 123.9 (2C), 127.9 (2C), 129.5 (2C), 134.5 (2C), 135.1 (2C), 146.0 (2C). ^{29}Si NMR: δ -2.00. MS (APCI): m/z (M + 1) 297.1. HRMS (APCI): m/z calc'd for [M + H]$^+$ C$_{18}$H$_{25}$Si$_2$ 297.1489, found 297.1487.

Conclusion

In conclusion, we have shown that the dimerization of silacyclobutanes is possible with a palladium catalyst at room temperature. The initial oxidative addition of palladium to the silacyclobutane is sensitive to the steric bulk at silicon, but the insertion into the second molecule of silacyclobutane is not. It is proposed that palladium colloids are formed under the reaction conditions which catalyze this process.

Acknowledgements

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