Palladium-catalysed three-component coupling reactions of dimethylsilacyclobutane, carbon monoxide and organic halides: a convenient route to cyclic silyl enol ethers

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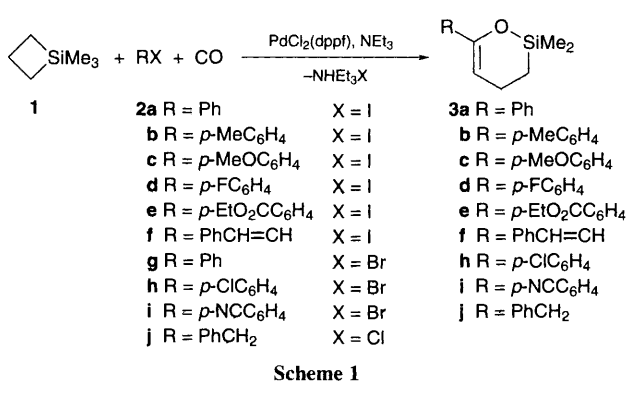
A facile one pot synthesis of cyclic silyl enol ethers, 1-sila-2-oxacyclohex-3-enes has been achieved by coupling reactions of strained 1,1-dimethyl-1-silacyclobutane with organic halides in CO atmosphere (1 atm) in the presence of palladium catalysts.

The ring strain [1] and/or Lewis acidity[2] of silacyclobutanes have been exploited to obtain ring expanded products with carbenes,[3] phosphorus ylides,[4] sulfur,[5] acetylenes and allenes.[6] Recently we reported oxidative addition of Si–C bonds of silacyclobutanes to Pt(0) complexes and highly selective Pt(0)-catalysed di- or poly-merization of 1,1-dimethyl-1-silacyclobutane **1**.[7] It was also revealed that silacyclobutanes reacted very smoothly with acid chlorides in the presence of palladium or platinum catalysts to furnish 3-(chlorosilyl)propyl ketones, which in the presence of amines could cyclize to a novel class of silyl enol ethers, oxasilacyclohexenes.[8] Silyl enol ethers have been those compounds of silicon to show major synthetic use.[9] We describe herein a one step synthesis of cyclic silyl enol ethers in excellent yields by coupling reactions of 1,1-dimethyl-1-silacyclobutane with organic halides in CO atmosphere (1 atm) in the presence of palladium catalysts.

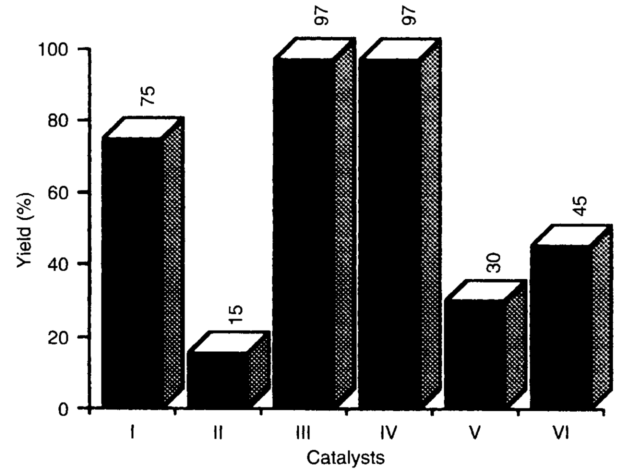
In a Schlenk tube $PdCl_2(dppf)$ [0.08 mmol, dppf = 1,1′-bis(diphenylphosphino)ferrocene] was stirred in 2.5 cm^3 of toluene under nitrogen and iodobenzene **2a** (2 mmol), triethylamine (4 mmol) and finally **1** (2 mmol) were injected into this solution. This mixture was degassed by 3–4 freeze-pump-thaw cycles and kept in an oil bath at 80 °C under atmospheric pressure of CO. Monitoring the reaction by ^1H, ^{29}Si and ^{13}C NMR indicated complete consumption of **1** (^{29}Si δ + 18.69) and formation of 1,1-dimethyl-3-phenyl-1-sila-2-oxacyclohex-3-ene **3a** (^{29}Si δ + 18.20) as sole product after 3 h. The solvent was removed under reduced pressure (6 mmHg) and the residue was mixed with hexane and the ammonium salt was filtered off. The filtrate was concentrated *in vacuo* and the residual oil was subjected to Kugelrohr distillation (116 °C/6 mmHg) to give analytically pure **3a** as a colourless oil in 93% yield (Scheme 1).



Scheme 1

A comparative study of the related $PdCl_2L_2$ complexes under identical reaction conditions to catalyse the coupling reaction of **1** with **2a** and CO (1 atm) revealed that palladium catalysts with comparatively basic phosphine ligands (PBu_3) or chelating alkyl phosphine ligands such as dppb [dppb = 1,4-bis(diphenylphosphino)butane] were less active than those with less basic ligands such as PPh_3, dpaf [dpaf = 1,1′-bis(diphenylarsino)-ferrocene] and dppf. Phosphine free systems such as $PdCl_2(PhCN)_2$ were also found to be active (Fig. 1).

The three component reaction proved to be equally applicable to other aromatic iodides containing either electron-releasing or electron-withdrawing substituents at the *para*-position. The results are summarized in Table 1.† *p*-Iodotoluene **2b**, *p*-iodoanisole **2c**, *p*-fluoroiodobenzene **2d** and ethyl *p*-iodo-



I: $PdCl_2(PPh_3)_2$, **II**: $PdCl_2(PBu_3)_2$, **III**: $PdCl_2(dpaf)$
IV: $PdCl_2(dppf)$, **V**: $PdCl_2(dppb)$, **VI**: $PdCl_2(PhCN)_2$

Fig. 1 Comparison of catalytic activity of palladium complexes

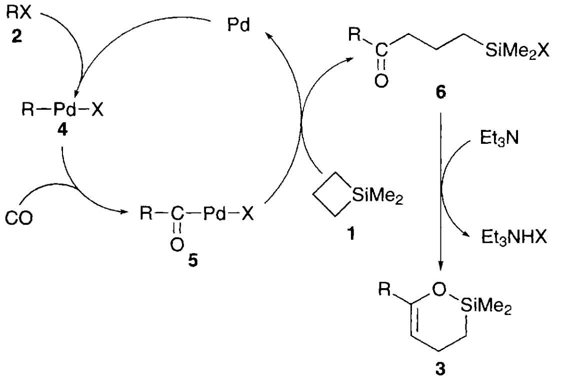
Table 1 Reaction of dimethylsilacyclobutane **1** with organic halides **2** and CO catalysed by $PdCl_2(dppf)$[a]

Run	RX 2	*T*/°C	*t*/h	Yield of **3** (%)[b,c]
1	**2a**	80	3	97 (93)
2	**2b**	80	5	94
3	**2c**	80	3	92 (90)
4	**2d**	80	3	93 (88)
5	**2e**	80	3	99 (92)
6	**2f**	80	3	97 (92)
7	**2g**	80	20	26
8	**2g**	120	20[d]	35
9	**2h**	80	24	76
10	**2i**	80	20	96 (92)

[a] Reaction conditions: **1** (2 mmol), **2** (2 mmol), Et_3N (4 mmol) $PdCl_2(dppf)$ (0.08 mmol), toluene (2.5 cm^3), CO (1 atm). [b] Estimated by ^1H NMR. [c] Figures in parentheses indicate the isolated yields. [d] CO 18 atm.

benzoate **2e** reacted with **1** to afford corresponding cyclic silyl enol ethers **3b–e** in excellent yields. Olefinic iodides such as β-iodostyrene **2f** also reacted with **1** under similar reaction conditions to furnish **3f** in high yield. In an attempt to improve the utility of the methodology, coupling reactions of **1** with aromatic chlorides and bromides under CO atmosphere were examined. In the presence of the $PdCl_2$(dppf) catalyst no reaction was observed with chlorobenzene, but bromobenzene **2g** did react with **1** to give **3a** in 26% yield. Extension of the reaction time did not significantly improve the outcome of the reaction. When a higher temperature (120 °C) and a higher pressure of CO (18 atm)‡ were employed, desired product **3a** could be obtained in 35% yield. Interestingly, unlike the parent bromobenzene being rather reluctant, *p*-bromochlorobenzene **2h** and *p*-bromobenzonitrile **2i** reacted smoothly with **1** under the standard reaction conditions (80 °C, CO 1 atm) to give 1,1-dimethyl-3-(4-chlorophenyl)-1-sila-2-oxacyclohex-3-ene **3h** and 1,1-dimethyl-3-(4-cyanophenyl)-1-sila-2-oxacyclohex-3-ene **3i** respectively in good yields. The presence of electron-withdrawing groups at the *para*-position may account for the increased reactivity of these halides. Benzyl chloride also appeared to undergo the coupling with **1** to form the corresponding silyl enol ether **3j** (25%) after 20 h reaction time as judged by ^{29}Si (δ 19.7 in C_6D_6) and ^{1}H NMR [δ 4.12 (=CH) and 0.16 ($SiCH_3$) in C_6D_6]. However, owing to byproduct formation, the structure could not be confirmed.

Based on our recent work[7,8] and precedents of palladium-catalysed carbonylation reactions of organic halides,[10] the present catalysis is best explained by the sequence of events depicted in Scheme 2. Thus oxidative addition of an organic halide generates an alkyl- or aryl-palladium species **4**, which undergoes CO insertion to give an acylpalladium intermediate **5**. Silacyclobutane **1** then interacts with intermediate **5** to furnish γ-(chlorosilyl)propyl ketone **6** which cyclizes in the presence of an amine to afford **3**. The observed reactivity trends PhI > PhBr ≫ PhCl and *p*-XC_6H_4Br > PhBr (X = electron-withdrawing substituents) are in good agreement with those reported for known carbonylation reactions and are associated with the ease of the initial oxidative addition of the halides.



Scheme 2 Catalytic cycle. Only actively reacting ligands are illustrated.

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Footnotes

† All products gave satisfactory spectral and/or elemental analysis data. *Selected data* for **3e**: ^{1}H NMR (300 Mz, C_6D_6): δ 0.16 (s, 6 H, $SiCH_3$), 0.61 (t, *J* = 7.02 Hz, 2 H, $SiCH_2$), 1.06 (t, *J* = 7.03 Hz, 3 H, CH_3) 2.24 (dt, *J* = 4.8 and 7.01 Hz, 2 H, CH_2), 4.14 (q, *J* = 6.9 Hz, 2 H, OCH_2), 5.35 (t, *J* = 4.9 Hz, 1 H, =CH), 7.62 (d, 2 H, C_6H_5), 8.12 (d, 2 H, C_6H_5); GC–MS *m/z* (relative intensity) 276 (56, M$^+$), 261 (28), 248 (11), 247 (47), 231 (16), 204 (19), 203 (100). For **3h**: ^{1}H NMR (300 Mz, C_6D_6): δ 0.19 (s, 6 H, $SiCH_3$), 0.56 (t, *J* = 7.02 Hz, 2 H, CH_2Si), 2.5 (dt, *J* = 4.8 and 7.01 Hz, 2 H, CH_2), 5.18 (t, *J* = 4.8 Hz, 1 H, =CH), 6.69–7.61 (m, 4 H, C_6H_4); ^{29}Si NMR (59.6 Mz, C_6D_6): δ 18.45. For **3i**: ^{1}H NMR (300 Mz, C_6D_6): δ 0.18 (s, 6 H, $SiCH_3$), 0.57 (t, *J* = 7.1 Hz, 2 H, CH_2Si), 2.21 (dt, *J* = 4.7 and 7.1 Hz, 2 H, CH_2), 5.23 (t, *J* = 4.9 Hz, 1 H, =CH), 6.79–7.73 (m, 4 H, C_6H_4); ^{29}Si NMR (59.6 Mz, C_6D_6): δ 19.1; GC–MS *m/z* (relative intensity) 229 (100, M$^+$), 228 (54), 214 (89), 201 (12), 186 (10), 155 (72).

‡ This reaction was performed in an autoclave.

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