Palladium- and Platinum-Catalyzed Reactions of Silacyclobutanes with Acid Chlorides Affording Cyclic Silyl Enol Ethers and/or 3-(Chlorosilyl)propyl Ketones

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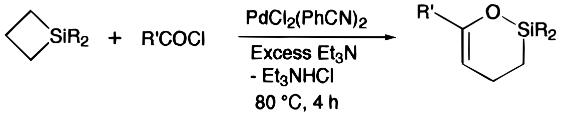
Summary: Palladium and platinum complexes catalyze the reaction of silacyclobutanes with acid chlorides in the presence of a large excess of a tertiary amine (triethylamine, diisopropylethylamine) at higher temperatures (∼80 °C) to give cyclic silyl enol ethers, 1-sila-2-oxa-3-cyclohexenes, in excellent yields, while the reaction in the presence of a limited quantity of the amine at room temperature forms 3-(chlorosilyl)propyl ketones in good yields.

Silacyclobutanes (**1**) are an interesting class of compounds that are able to undergo a variety of reactions based on their ring strain[1] and/or Lewis acidity.[2] Particularly useful reactions are those promoted by metal complex catalysts such as ring-opening polymerization[3] and cycloaddition reactions with acetylenes and allenes.[4] We also reported previously that Pt(0) species catalyzed dimerization and/or polymerization of 1,1-dimethyl-1-silacyclobutane (**1a**), depending on the structure of the catalyst. In addition, **1** was found to undergo oxidative-addition reactions with Pt(0) complexes to form 1-platina-2-silacyclopentane complexes.[5] Continued research along these lines has revealed that the palladium-catalyzed reaction of **1** with acid chlorides (**2**) proceeds smoothly in the presence of tertiary amines to give unique cyclic silyl enol ethers (**3**) in high yields.

To a stirred solution of $PdCl_2(PhCN)_2$ (0.08 mmol) in toluene (2 mL) were added, under nitrogen, benzoyl chloride (**2a**, 2 mmol), triethylamine (4 mmol), and then **1a** (2 mmol), and the resulting mixture was stirred at 80 °C for 4 h. Monitoring the reaction by ^1H, ^{13}C, and ^{29}Si NMR revealed that 1,1-dimethyl-3-phenyl-1-sila-2-oxa-3-cyclohexene (**3a**)[6] was formed in 43 (0.5 h), 71 (1 h), 93 (2 h), and 97% (4 h) yields.[7] After removal of the solvent under reduced pressure, the residue was mixed with hexane and the ammonium salt was filtered off. The filtrate was concentrated *in vacuo*, and the residual oil was purified by Kugelrohr distillation to give analytically pure **3a** as a colorless oil (eq 1).



(1)

$PdCl_2(PPh_3)_2$ also catalyzed the foregoing reaction to give **3a**, although the reaction was slower (0.5 h, 9% yield; 2 h, 46%; 4 h, 83%).[7,8]

As anticipated from mechanistic considerations (*vide infra*), the reaction could be promoted by a platinum complex, $Pt(CH_2{=}CH_2)(PPh_3)_2$, but its performance was inferior to that of the palladium complexes. Thus, the reaction between **1a** and **2a** by the same procedure at 80 °C (for the first 2 h) up to 100 °C (thereafter) gave **3a** and **4a** in 6 and 4% (80 °C, 2 h), 29 and 4% (100 °C, additional 2 h), 42 and 4% (100 °C, additional 2 h), and 87 and 5% (100 °C, additional 10 h) yields,[7] respectively.

Selected results are summarized in Table 1. In the presence of triethylamine and $PdCl_2(PhCN)_2$, aromatic and heteroaromatic acid chlorides **2a**−**e** reacted with **1a** to afford **3a**−**e**[6] in high yields. Cinnamoyl chloride (**2f**) smoothly reacted with **1a** to give the cyclic silyl dienol ether (**3f**)[6] in 97% yield. Cyclohexanecarbonyl chloride (**2g**) also reacted with **1a** to give **3g**[6] in 94% yield. The only acid chloride that did not afford **3** under the same conditions was heptanoyl chloride (**2h**), a linear acid chloride. When treated with triethylamine in toluene at room temperature, it was readily converted to the corresponding ketene dimer, which was confirmed to be unreactive toward **1a** under the catalytic reaction conditions. The ketene dimer formation is expected to be less serious when more hindered amines are used.[9] Reactions of linear acid chlorides run in the presence of diisopropylethylamine in place of triethylamine in-

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[1] The strain energies of silacyclobutane, silacyclopentane, and silacyclohexane are 102.5, 20.1, and 13.0 kJ mol^{-1}, respectively. See: Gordon, M. S.; Boatz, J. A.; Walsh, R. *J. Phys. Chem.* **1989**, *93*, 1584.

[2] (a) For "strain release Lewis acidity" of silacyclobutanes, see: Denmark, S. E.; Griedel, B. D.; Coe, D. E.; Schnute, M. E. *J. Am. Chem. Soc.* **1994**, *116*, 7026. (b) See also: Matsumoto, K.; Oshima, K.; Utimoto, K. *J. Org. Chem.* **1994**, *59*, 7152.

[3] (a) Weyenberg, D. R.; Nelson, L. E. *J. Org. Chem.* **1965**, *30*, 2618. (b) Nametkin, N. S.; Ushakov, N. V.; Vdovin, V. M. *Vysokomol. Soedin., Ser. A* **1971**, *13*, 29; *Chem. Abstr.* **1971**, *74*, 88325w. (c) Cundy, C. S.; Eaborn, C.; Lappert, M. F. *J. Organomet. Chem.* **1972**, *44*, 291 and references cited therein. (d) Poletaev, V. A.; Vdovin, V. M.; Nametkin, N. S. *Dokl. Akad. Nauk SSSR* **1973**, *208*, 1112; *Chem. Abstr.* **1973**, *79*, 19191r. (e) Finkel'shtein, E. Sh.; Ushakov, N. V.; Pritula, N. A.; Andreev, E. A.; Plate, N. A. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1992**, *223*; *Chem. Abstr.* **1992**, *116*, 256191f. (f) Ushakov, N. V.; Yarysheva, A. Yu.; Tal'roze, R. V.; Finkel'shtein, E. Sh.; Plate, N. A. *Dokl. Akad. Nauk* **1992**, *325*, 964; *Chem. Abstr.* **1993**, *118*, 102788k. (g) Bialecka-Florjanczyk, E.; Ganicz, T.; Stanczyk, W.; Sledzinska, I. *Polimery (Warsaw)* **1993**, *38*, 424; *Chem. Abstr.* **1994**, *121*, 36351w. (h) Liao, C. X.; Chen, M. W.; Sun, L.; Weber, W. P. *J. Inorg. Organomet. Polym.* **1993**, *3*, 231.

[4] Sakurai, H.; Imai, T. *Chem. Lett.* **1975**, 891. Takeyama, Y.; Nozaki, K.; Matsumoto, K.; Oshima, K.; Utimoto, K. *Bull. Chem. Soc. Jpn.* **1991**, *64*, 1461.

[5] Yamashita, H.; Tanaka, M.; Honda, K. *J. Am. Chem. Soc.* **1995**, *117*, 8873.

[6] Compounds **3a**−**j**, **3a′**, and **3b′** were isolated by Kugelrohr distillation. Compounds **3a**−**j**, **3a′**, and **3b′** showed satisfactory ^1H, ^{13}C, and ^{29}Si NMR, IR, (HR)MS, and/or analytical data (see Supporting Information). For example, ^1H and ^{29}Si NMR spectral data for **3a** in C_6D_6 are as follows. **3a**: ^1H NMR δ 0.15 (s, 6H, $SiCH_3$), 0.63 (t, J = 7.1 Hz, 2H, CH_2Si), 2.27 (dt, J = 4.9 and 7.1 Hz, 2H, CH_2), 5.39 (t, J = 4.9 Hz, 1H, =CH), 7.07−7.80 (m, 5H, C_6H_5); ^{29}Si NMR δ 18.2.

[7] Quantification is based on integration of ^1H NMR signals assignable to Si−CH_3 protons of **1a** (0.18 ppm), **3a** (0.15 ppm), and/or **4a** (0.22 ppm); error limits are ±2%.

[8] The reaction was accompanied by the formation of unknown compounds (4 h, ∼9% yield).

[9] We thank one of the reviewers for this suggestion.

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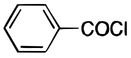
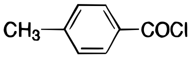
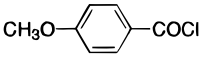
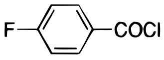
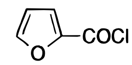
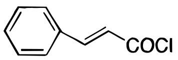
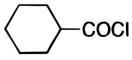
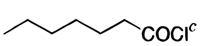
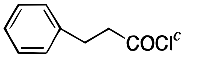
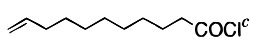
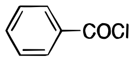
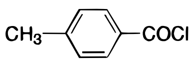
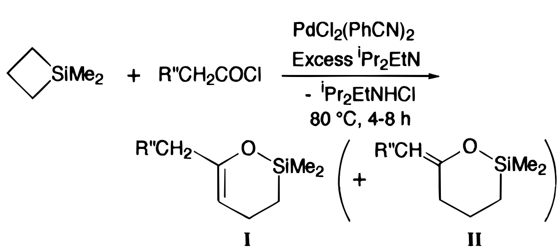
Table 1. Reaction of Silacyclobutanes 1 with Acid Chlorides 2 Catalyzed by $PdCl_2(PhCN)_2$[a]

1	acid chloride (2)		yield of 3/%[b]
1a		**2a**	97 (92)
1a		**2b**	93 (88)
1a		**2c**	99 (94)
1a		**2d**	98 (92)
1a		**2e**	86 (81)
1a		**2f**	97 (75)
1a		**2g**	94 (90)
1a	 [c]	**2h**	96 (91)[d]
1a	 [c]	**2i**	79 (73)[d, e]
1a	 [c]	**2j**	95 (90)[d]
1b		**2a**	98 (91)[f]
1b		**2b**	95 (90)

[a] Reaction conditions: **1** (2 mmol), **2** (2 mmol), Et_3N (4 mmol), $PdCl_2(PhCN)_2$ (0.08 mmol), in toluene (2 mL), 80 °C, 4 h. [b] Estimated by ^1H NMR. Figures in parentheses indicate isolated yields. [c] Reactions were performed in the presence of $^iPr_2NEt$ (4 mmol) instead of Et_3N. [d] Mixture of two isomers (See eq 3): **I**/**II** = 85/15 - 83/17 (**I**: 3-alkyl-1-sila-2-oxa-3-cyclohexene. **II**: 3-alkylidene-1-sila-2-oxacyclohexane). [e] Reaction time, 8 h. [f] Reaction time, 2 h.

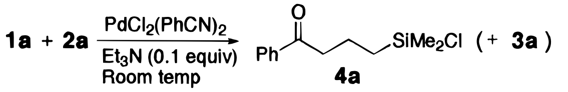
deed worked nicely to give isomeric mixtures of the corresponding silyl enol ethers in good total yields (eq 2).



(2)

1,1-Diphenyl-1-silacyclobutane (**1b**) also reacted with **2a** and **2b** under identical conditions to give the cyclic silyl enol ethers **3a′**[6] (0.5 h, 54%; 2 h, 98%) and **3b′**[6] (4 h, 95%),[10] respectively, in spite of its increased steric hindrance. On the other hand, 1,1-dimethyl-1-silacyclopentane and 1,1-dimethyl-1-silacyclohexane did not react even at a higher temperature (120 °C), presumably because of their nearly strain-free ring system.[1]

As described in the previous section, the catalysis worked efficiently in the presence of a large excess of a tertiary amine. In the absence of the amines, an attempted catalytic reaction between **1a** and **2a** under the standard catalytic reaction conditions gave only a 2.5% yield of **3a**,[7] indicating that the reaction was, in reality, not catalytic; note that the quantity of the catalyst was 4 mol % relative to **1a**.[11] However, the reaction did proceed catalytically even at room temperature when it was effected *in the presence of a minute quantity of triethylamine* (0.1 equiv). Under the modified conditions 1-phenyl-4-(chlorodimethylsilyl)-1-butanone (**4a**)[12] was formed as the major product (86% NMR yield) in 2 h along with a small amount of **3a** (7% NMR yield),[7] as shown in eq 3. This modified procedure



(3)

thus provides another useful variation of the catalytic reaction between **1a** and acid chlorides to synthesize γ-silylalkyl ketones in good yields. Note that hydrosilylation of β,γ- or γ,δ-unsaturated carbonyl compounds does not appear to selectively form γ-silylalkyl ketones but usually results in nonselective formation of a mixture of products arising from 1,2-addition to both C=C and C=O double bonds (and also 1,4-addition).[13]

When the time course of the catalytic reaction between **1a** and **2a** (2 equiv) under normal conditions (*i.e.*, in the presence of a large excess of triethylamine) was carefully followed by ^1H NMR, compound **4a** could be detected as a transient intermediate that appeared in the early stages (0.5 h, 50%; 1 h, 26%; 2 h, 5%; 4 h, 0%).[7] The base-assisted reaction between chlorosilanes and enolizable carbonyl compounds is the standard method to prepare silyl enol ethers. Indeed, **4a** cyclized to give **3a** in a nearly quantitative yield when heated in the presence of 2 equiv of triethylamine in toluene at 80 °C for 1 h. Accordingly, the catalytic formation of **3a** is envisioned to occur through the cyclization of **4a**.

The intermediates **4** were also observed in the reactions with other acid chlorides. With regard to the formation mechanism of **4**, one can envision two alternative intermediates; one is a 1-pallada-2-silacyclopentane species (**5**),[4] and the other is a chloro(acyl)palladium species (**6**; Scheme 1). On the basis of the following observations, the latter (path B) appears more likely. Thus, $PhCOPdCl(PPh_3)_2$ (**6a**; 0.1 M in benzene-d_6) was treated with **1a** (1.1 equiv) in the absence of

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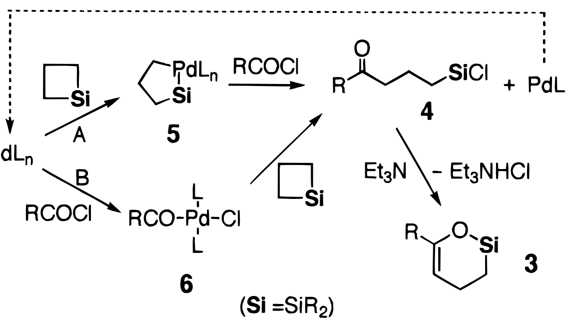
(10) Yields were determined by integration of ^1H NMR signals assignable to CH_2Si of **1b** (1.49 ppm) and the vinylic CH of **3a′** (5.43 ppm) or **3b′** (5.44 ppm); error limits are ±4%.

(11) It is well recognized that palladium-catalyzed hydrogen halide generating reactions such as the Heck reactions do not work unless amines (or other hydrogen halide acceptors) are present in the reaction system. This is because the catalyst is regenerated by the reaction of amines that re-form palladium(0) species. For instance, see: (a) Crabtree, R. H. *The Organometallic Chemistry of the Transition Metals*; Wiley-Interscience: New York, 1994; p 396. (b) Heck, R. F. *Palladium Reagents in Organic Synthesis*; Academic Press: London, UK, 1985; p 276.

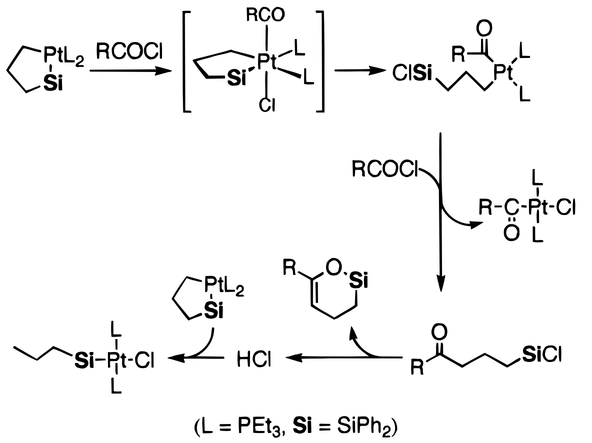
(12) **4a**: ^1H NMR (C_6D_6) δ 0.22 (s, 6H, $SiCH_3$), 0.60–0.69 (m, 2H, CH_2Si), 1.67–1.82 (m, 2H, CH_2), 2.58 (t, J = 7.0 Hz, 2H, $COCH_2$), 7.10–7.88 (m, 5H, C_6H_5); ^{29}Si NMR (C_6D_6) δ 31.6.

(13) Marciniec, B., Ed. *Comprehensive Handbook on Hydrosilylation*; Pergamon: Headington Hill Hall, UK, 1992; pp 145–150.

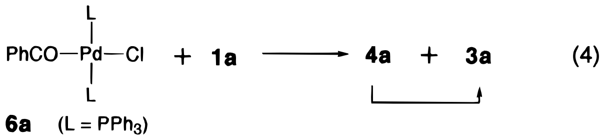
Scheme 1



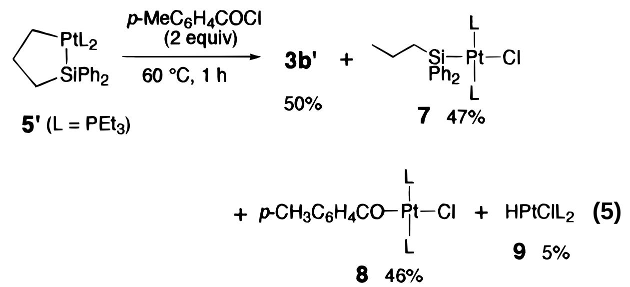
Scheme 2



the amine at 60−120 °C in a sealed NMR tube. NMR of the reaction mixture indeed revealed formation of **3a**, *via* the intermediate **4a**: 60 °C, 2 h, **3a** 19%, **4a** 50%; 80 °C, additional 2 h, **3a** 38%, **4a** 50%; 120 °C, additional 1 h, **3a** 87%, **4a** 7% (eq 4),[7] suggesting catalysis *via* path B.



On the other hand, to look into the possibility of the alternative mechanism (path A), we attempted to synthesize the 1-pallada-2-silacyclopentane species (**5**). We have been unsuccessful at obtaining it to date (*vide infra*). Instead, we treated a toluene-d_8 solution of the 1,1-bis(triethylphosphine)-2,2-diphenyl-1-platina-2-silacyclopentane complex[5] (**5′**; 0.1 M) with **2b** (2 equiv) in the absence of the amine at 60 °C for 1 h in a sealed NMR tube; note that a platinum complex was also catalytically active (*vide supra*). ^{1}H, ^{13}C, ^{29}Si, and ^{31}P NMR of the reaction mixture showed formation of the corresponding cyclic silyl enol ether (**3b′**) in 50% yield along with several platinum complexes (eq 5).[14] The result is reasonably explained by the sequence of events depicted in Scheme 2 and is not totally at odds with path A. However, the following observations that indicate **1a** is much less reactive toward low-valent transition metal complexes than are acid chlorides provide strong evidence against path A. Thus, when a mixture of **1a** or **1b** (0.125 mmol), **2a** (0.125 mmol), and benzene-d_6 (0.25 mL) was added to $Pd(PPh_3)_4$ (0.125 mmol) in a sealed NMR tube, $PhCOPdCl(PPh_3)_2$ was nearly quantitatively formed as the sole product in 15 min at ambient temperature, while **1a** or **1b** remained intact.[16] $Pt(PEt_3)_3$ (0.125 mmol) used in place of $Pd(PPh_3)_4$ behaved very similarly to give only $PhCOPtCl(PEt_3)_2$.[17] In strong contrast with these stoichiometric reactions of Pd(0) and Pt(0) complexes, compound **4a** could be catalytically formed even at room temperature (eq 3). Finally, it is interesting to note that, in any of the catalytic reactions with acid chlorides, we did not find 1,1,5,5-tetramethyl-1,5-disilacyclooctane, a dimer of **1a**, formed as a byproduct. Since $Pt(CH_2{=}CH_2)(PPh_3)_2$ is quite active in the dimerization of **1a**,[5] the dimer formation could have resulted at least in the Pt-$(CH_2{=}CH_2)(PPh_3)_2$-catalyzed reaction if the catalysis were initiated by the generation of a five-membered intermediate such as **5′**. Accordingly, the possibility of path A playing an important role in the catalysis appears less likely, even though it is not rigorously excluded.



In conclusion, the reaction of silacyclobutanes with acid chlorides offers a novel and high-yield synthesis of a new class of cyclic silyl enol ethers (1-sila-2-oxa-3-cyclohexenes) or γ-(chlorosilyl)propyl ketones.

Supporting Information Available: Text giving experimental details for the synthesis of **3a** and **4a**, synthetic procedures to prepare authentic samples of **7** and **8**, and ^{1}H, ^{13}C, and ^{29}Si and/or ^{31}P NMR, IR, MS, and analytical data for **3a**−**j**, **3a′**, **3b′**, **4a**, **7**, and **8** (7 pages). Ordering information is given on any current masthead page.

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[14] A mixture of **5′**[8] (0.03 mmol), **2b** (0.06 mmol), and toluene-d_8 (0.3 mL) in a nitrogen-purged, sealed NMR tube was heated at 60 °C for 1 h. The resulting mixture did not exhibit ^{31}P NMR signals centered at 7.5 and 16.7 ppm due to **5′**, indicative of completion of the reaction; instead, new signals emerged at 13.5, 16.4, and 23.2 ppm. Preparation of authentic samples confirmed that the first two signals were due to **7** and **8**, and the last one was safely assigned to **9** by comparison with literature data (including of ^{1}H NMR).[15] ^{1}H NMR showed that **7** (47%, integration of CH_2Si signal at 1.07 ppm), **8** (46%, integration of p-CH_3 signal at 2.04 ppm), and **9** (5%, integration of H−Pt sigral at −16.91 ppm) were formed in addition to **3b′** (50%, integration of the vinylic H signal at 5.44 ppm).

[15] (a) Socrates, G. *J. Inorg. Nucl. Chem.* **1969**, *31*, 1667. (b) Parshall, G. W. *Inorg. Synth.* **1970**, *12*, 26.

[16] No reaction took place, even when a mixture of **1b** and $Pd(PPh_3)_4$ in benzene-d_6 was heated at 140 °C.

[17] Note that the reactions of **1a** and **1b** with $Pt(PEt_3)_3$ in the absence of acid chlorides form the five-membered complexes only when the temperature is raised to 90 °C.[5]