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Oxidative Addition of the Si−C Bonds of Silacyclobutanes to $Pt(PEt_3)_3$ and Highly Selective Platinum(0)-Catalyzed Di- or Polymerization of 1,1-Dimethyl-1-silacyclobutane

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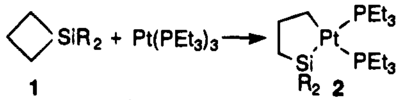
Organosilicon polymers have attracted growing attention for their unique physicochemical properties.[1] Ring-opening polymerization (ROP) of silacycles is a most promising method to prepare these silicon polymers.[2] Group 9 or 10 metal-catalyzed ROP of carbosilacycles[3] in particular has been effectively used for the synthesis of silylene and methylene unit-containing polycarbosilanes, which have recently been refocused for their applicability to the synthesis of functionalized polycarbosilanes[2c,d] or SiC ceramics.[2d] In the reactions of silacyclobutanes, activation of the Si−C bonds by catalyst species was proposed as a key elemental step.[4] However, persuasive evidence is still lacking. Herein we report that the Si−C bonds of silacyclobutanes readily undergo oxidative addition to $Pt(PEt_3)_3$ to form 1-platina-2-silacyclopentane complexes.[5] In addition, the new finding has led to the development of highly selective di- or polymerization of a silacyclobutane, depending on the structure of the platinum(0) catalyst.



(1)

a: R =Ph, **b**: R = Cl, **c** : R = Me

When a mixture of $Pt(PEt_3)_3$ (0,327 mmol), 1,1-diphenyl-1-silacyclobutane (**1a**, 2,5 equiv), and toluene-d_8 (0,24 mL) was heated in a sealed NMR tube (60 °C, 10 min + 90 °C, 100 min), the color of the solution turned from orange to pale yellow. ^{31}P NMR revealed clean conversion of $Pt(PEt_3)_3$ (41.5 ppm) into a 1-platina-2-silacyclopentane species (**2a**; 7.5, 16,7 ppm) with extrusion of a PEt_3 molecule (−19 ppm) (eq 1). ^1H NMR monitoring showed that the yields (temperature, reaction time) were ~20% (60 °C, 10 min), ~90% (90 °C, additional 40 min), and ≥95% (90 °C, additional 60 min). Concentration of the reaction mixture in vacuo, followed by recrystallization from toluene−hexane, gave pure **2a**[6a] (0,274 mmol, 84% yield) as colorless prismatic crystals. The structure was unequivocally confirmed by X-ray diffraction,[7] verifying the oxidative addition of the ring's Si−C bond of **1a** to $Pt(PEt_3)_3$. Species **2a** has a slightly distorted square-planar coordination geometry, with the Pt−Si and Pt−C bond lengths (Å) being 2.354(1) and 2.132(4), respectively. The Pt−P bond lengths (Å) are 2.368(1) (P trans to Si) and 2.301(1) (P trans to C), showing that the silyl ligand exerts stronger trans influence than the alkyl ligand.

1,1-Dichloro-1-silacyclobutane (**1b**, 2.5 equiv) reacted similarly with $Pt(PEt_3)_3$ even at room temperature to give the corresponding adduct **2b** in ~90% NMR yield within 1 h, although a small quantity (~10%) of a Si−Cl addition product, *trans*-$\overline{CH_2(CH_2)_2ClSi}PtCl(PEt_3)_2$, was also formed. The reaction of 1,1-dimethyl-1-silacyclobutane (**1c**, 2.5 equiv) proceeded at 60−90 °C as well to form the corresponding complex (**2c**) in ~45% NMR yield (60 °C, 10 min + 90 °C, 40 min). Further heating (60 min) did not substantially increase the yield, indicating that $Pt(PEt_3)_4$, which was generated from $Pt(PEt_3)_3$ and the free PEt_3 extruded in the formation of **2c**, was nearly unreactive toward **1c**. Although pure samples of species **2b,c** were not obtained, their NMR spectra[6b,c] were fully consistent with the postulated structures. On the basis of the reaction conditions and the yields, the reactivity of **1a**−**c**, $\overline{CH_2(CH_2)_2Si}R_2$, increases in the order of R = Me < Ph < Cl, suggesting that electron-withdrawing substituents are favorable for the reaction. On the other hand, a nearly strain-free six-membered silacycle, 1,1-dimethyl- or 1,1-dichloro-1-silacyclohexane, did not undergo oxidative addition of the Si−C bond (120 °C, 30 min or ~90 °C, 100 min, respectively).[8] Apparently, the ring strain of silacyclobutanes is a driving force of the reaction.[9]

In the foregoing reaction of **1c**, its dimer, 1,1,5,5-tetramethyl-1,5-disilacyclooctane (**3**), was also formed along with **2c**. Dimer **3** increased after the formation of **2c**, and the yield of **3** exceeded 100% based on **2c**; the NMR yields of **3** and **2c** (temperature, reaction time) were respectively ~0 and ~5% (60 °C, 10 min), ~50 and ~35% (90 °C, additional 10 min), ~140 and ~45% (90 °C, additional 30 min), and ~200 and ~45% (90 °C, additional 60 min). This suggests that **3** is formed catalytically via interaction of **2c** with **1c**. In fact, treatment of the Ph_2Si

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(6) Selected NMR data. (a) **2a**: ^{29}Si NMR ($CDCl_3$) δ 35.9 (dd, $^2J_{PSi}$ = 172, 14.5 Hz, $^1J_{PtSi}$ = 1421 Hz); ^{31}P NMR δ 7.4 (d, $^2J_{PP}$ = 18.9 Hz, $^1J_{PtP}$ = 1915 Hz, P trans to C), 16.8 (d, $^2J_{PP}$ = 18.9 Hz, $^1J_{PtP}$ = 1346 Hz, $^2J_{PSi}$ = 172 Hz, P trans to Si). (b) **2b**: ^{29}Si NMR ($C_6D_5CD_3$, −20 °C) δ 79.4 (dd, $^2J_{PSi}$ = 257, 19.3 Hz, $^1J_{PtSi}$ = 2061 Hz); ^{31}P NMR (−20 °C) δ 8.1 (d, $^2J_{PP}$ = 18.5 Hz, $^1J_{PtP}$ = 1943 Hz, P trans to C), 13.5 (d, $^2J_{PP}$ = 18.5 Hz, $^1J_{PtP}$ = 1699 Hz, $^2J_{PSi}$ = 257 Hz, P trans to Si). (c) **2c**: ^{29}Si NMR ($C_6D_5CD_3$) δ 34.6 (dd, $^2J_{PSi}$ = 163, 14.0 Hz, $^1J_{PtSi}$ = 1281 Hz); ^{31}P NMR δ 11.7 (d, $^2J_{PP}$ = 17.9 Hz, $^1J_{PtP}$ = 1966 Hz, P trans to C), 15.9 (d, $^2J_{PP}$ = 17.9 Hz, $^1J_{PtP}$ = 1180 Hz, $^2J_{PSi}$ = 163 Hz, P trans to Si).

(7) Crystal data for **2a**: $PtP_2SiC_{27}H_{46}$, monoclinic, space group $P2_1/n$, a = 16.647(3) Å, b = 19.057(2) Å, c = 9.410(2) Å, β = 97.37(2)°, V = 2960.7(8) Å^3, Z = 4, D_{calc} = 1.471 g cm^{-3}. The intensity data were collected with a Rigaku AFC7R diffractometer using Mo Kα radiation over the range of $3 \le 2\theta \le 50°$. Refinement to convergence of the 281 parameters on 4659 unique reflections with $I > 3.0\sigma(I)$ gave R (R_w) = 0.029 (0.040).

(8) Dimethylsilacyclohexane did not react, while the dichloro derivative reacted at the Si−Cl bond to give a chloro(silyl)platinum(II) complex like that formed from **1b** (60 °C, 10 min + 90 °C, 100 min, ~80% NMR yield).

(9) The ring strain (kcal/mol) of silacycles $\overline{CH_2(CH_2)_{n-2}Si}H_2$ was estimated at 3.1 (n = 6), 4.8 (n = 5), and 24.5 (n = 4). Gordon, M. S.; Boatz, J. A.; Walsh, R. *J. Phys. Chem.* **1989**, *93*, 1584.

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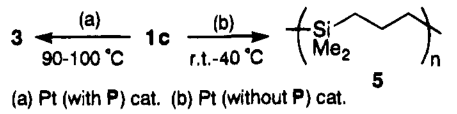
Table 1. Platinum-Catalyzed Dimerization of 1,1-Dimethyl-1-silacyclobutane (**1c**)[a]

run	catalyst	phosphine	P/Pt	yield (conversion)[b] (%)		
				10 min	120 min	420 min
1	$Pt(PEt_3)_3$	PEt_3	3	23 (25)	87 (93)	90 (≥99)
2	$Pt(CH_2{=}CH_2)(PPh_3)_2$	PPh_3	2	28 (35)	68 (76)	85 (94)
3	$Pt(CH_2{=}CH_2)(PPh_3)_2 + PPh_3$	PPh_3	3	7 (10)	57 (60)	[90 (95)][c]
4	$Pt(PPh_3)_4$	PPh_3	4		46 (46)	[96 (97)][d]
5[e]	$Pt(PPh_3)_4$	PPh_3	4			[97 (98)][f]

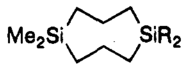
[a] **1c**, 0.80 mmol; catalyst, 5 mol % Pt; $C_6D_5CD_3$, 0.20 mL; 90 °C. [b] The yields were estimated by ^1H NMR. Small quantities (≤10%) of oligomeric compounds ($M_n \leq 1000$ by GPC) were also formed as byproducts. [c] 12 h. [d] 27 h. [e] Catalyst, 1 mol % Pt; C_6D_6, 0.20 mL; 100 °C. [f] 38 h. Isolated yield was 95%.

Scheme 1



(a) Pt (with P) cat. (b) Pt (without P) cat.

complex **2a** (~0.2 M toluene-d_8 solution) with the Me_2Si monomer **1c** (20 equiv) in the presence of PEt_3 (1 equiv)[10] at 90 °C for 3.5 h converted **2a** (≥95% by NMR) into 1,1-dimethyl-5,5-diphenyl-1,5-disilacyclooctane (**4**) in ~80%/Pt yield (by GC) along with **2c** (~50%) and **3** (≥1500%/Pt),

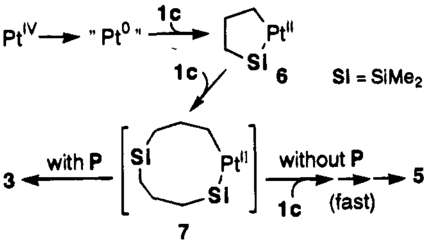


3: R = Me, **4**: R = Ph

The dimerization of **1c** was efficiently catalyzed by phosphine–platinum(0) complexes, yielding **3** in ≥85% NMR yields (Scheme 1, Table 1). Throughout the course of the reaction with the $Pt(PEt_3)_3$ catalyst, the 1-platina-2-silacyclopentane **2c** was observed by ^1H and ^{31}P NMR as the sole Si–Pt species, indicating the involvement of **2c** in the catalysis (vide supra). The PPh_3 complex was also effective, although its activity was lower than that of the PEt_3 complex (runs 1 and 3). In the series of PPh_3 complexes, an increase in the ratio of P/Pt retarded the reaction, whereas it improved the selectivity for **3** with suppression of oligomer formation (runs 2, 3, and 4); in the reaction of **1c** effected by $Pt(PPh_3)_4$ (1 mol %), **3** could be obtained in a high isolated yield (95%) by simple short-path distillation (run 5).

In accordance with the effect of the P/Pt ratio, the use of phosphine-free platinum complexes resulted in exclusive polymerization of **1c** (Scheme 1). Thus, treatment of **1c** (0.60 mmol) with a catalytic amount of $Pt(cod)_2$ (cod = 1,5-cyclooctadiene, Pt/**1c** = 1/50) in toluene-d_8 (0.15 mL) at room temperature (~18 °C) caused an exothermic reaction to form poly[trimethylene(dimethylsilylene)][3a] (**5**) with M_n = 36 000 (M_w/M_n = 2.1, by GPC with polystyrene standards) in a quantitative yield (after ~2 h, by NMR and GPC). Dimer **3** was not detected by NMR. The catalysis was extremely efficient, and even a trace amount of the complex (Pt/**1c** = 1/50 000) could promote the reaction at room temperature to selectively provide **5** with significantly higher molecular weight, M_n = 94 000 (M_w/M_n = 1.8) (~2 h, ~90% conversion). On the contrary, a conventional platinum catalyst, H_2PtCl_6 (Pt/**1c** = 1/50), hardly catalyzed the reaction at room temperature (~2 h), although a higher reaction temperature (40 °C) initiated the reaction to give **5** with M_n = 87 000 (M_w/M_n = 3.0) after 30 min heating. This indicates that reduction to a lower oxidation state than the Pt(IV) species must be integral in the early stages of the reaction.

Scheme 2



A conceivable initial intermediate in the di- or polymerization reaction is a 1-platina-2-silacyclopentane species (**6**) (Scheme 2); even in a phosphine-free system such as $Pt(cod)_2$ (Pt/**1c** = 1/50), a Me_2Si–Pt species could be clearly observed by NMR. For the H_3CSi–Pt signals: ^1H NMR δ 0.42 ($^3J_{PtH}$ = 32.6 Hz); ^{13}C NMR δ 1.7 ($^2J_{PtC}$ = 85.8 Hz); ^{29}Si NMR δ 32.4 ($^1J_{PtSi}$ = 1573 Hz). The five-membered intermediate **6** is likely to react with **1c** to give a 1-platina-2-silacyclononane (**7**), possibly via the Si–C bond addition and elimination process or via the four-center interaction between the Si–C and Pt–Si bonds. The resulting species **7** would be less stable owing to its larger ring size, forming the dimer **3** by reductive elimination, as observed in the phosphine–platinum catalysis. On the other hand, without phosphine ligands, the access of **1c** to the platinum center would take place much more easily, allowing successive interaction of **1c** with the platinasilacyclic intermediate to eventually give the polymer **5**.[11]

Supporting Information Available: Characterization data for **2a–c**, **3**, **4**, **5**, and *trans*-$\overline{CH_2(CH_2)_2ClSi}PtCl(PEt_3)_2$, including experimental procedures; a perspective view and tables of crystallographic data, atomic coordinates and thermal parameters, and bond lengths and angles for **2a** (15 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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(10) Without addition of PEt_3, the reaction did not proceed cleanly; the yield of **4** was ≤40% with ~80% conversion of **2a** (**1c**, 4 equiv; 60 °C, 40 min).

(11) There are two possible termination modes: one is β-hydride elimination, giving linear main chains with allylsilyl terminals,[4b] and the other is Si–C bond reductive elimination, resulting in cyclic main chains. The use of a reduced quantity of **1c** (**1c**, ~0.8 M; Pt/**1c** = 1/10; ~18 °C, ~2 h) gave **5** with a relatively low molecular weight (~50% NMR yield, M_n = ~15 000). In the NMR measurement of the reaction mixture, the signals for allylsilyl moieties were not observed, suggesting that the major part of **5** might be cyclic.