

## Preliminary communication

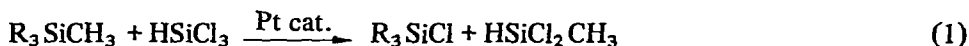
### A selective exchange of alkyl and chloro groups attached to silicon

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In the course of our investigation of the platinum-catalyzed hydrosilylation reaction, we have discovered a new and useful method for cleaving a carbon-silicon bond. Reported here is a series of reactions in which an alkyl group is cleaved from a silicon atom and replaced in turn by a chlorine atom derived from trichlorosilane. This exchange can be generally represented by eq. 1.



Thus, heating a mixture of 1.86 g (10 mmol) of *n*-octyltrimethylsilane, 1.5 ml (15 mmol) trichlorosilane, and *ca.* 15 mg of chloroplatinic acid ( $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ ) in a sealed 10 X 200 mm Pyrex tube at 151° for 8 h afforded on distillation 1.91 g (92%) of *n*-octyldimethylchlorosilane, b.p. 80–82° (2 mm) [lit. <sup>1</sup> b.p. 222–225°].

Data for several other reactions are summarized in Table 1.

Examination of the data in Table 1 reveals some very interesting aspects of the exchange reaction. Entries 1–3 demonstrate the generality of the cleavage of a silicon-methyl. In these, as well as the other reactions in which a methyl group is replaced, the other product is methyldichlorosilane. Ethyldichlorosilane is the product from an ethyl-chlorine exchange (entry 4, Table 1).

If the smallest moiety attached to the organosilane is an ethyl group, it is exchanged in the same manner as in the methyl cases. Entry 5 reveals the most striking aspect of the reaction. A silicon-methyl can be selectively and quantitatively exchanged for a silicon-chlorine, even in the presence of an ethyl moiety. This selectivity is quite amazing considering the small difference in steric requirements and electronic factors between a methyl and an ethyl group.

Electron-withdrawing groups (phenyl) or atoms (chlorine and oxygen) attached to the silicon atom bearing the methyl moiety definitely retard the exchange (entries 6–10). Two such substituents on the same silicon atom completely impede further exchange (entries 7 and 9). Further work will be necessary to ascertain whether this specificity is simply a rate effect or whether the products obtained represent the most thermodynamically stable species under the reaction conditions employed.

It is interesting to note the variety of platinum complexes which catalyze the

TABLE 1

## SELECTIVE ALKYL-CHLORINE EXCHANGE IN ORGANOSILANES BY TRICHLOROSILANE AND CHLOROPLATINIC ACID

Reactant	Product <sup>b</sup>	Conditions <sup>a</sup>
1 Me <sub>4</sub> Si	Me <sub>3</sub> SiCl (97%) <sup>d</sup>	157°, 24 h 20 mg H <sub>2</sub> PtCl <sub>6</sub>
2 Me <sub>3</sub> Si(CH <sub>2</sub> ) <sub>6</sub> SiMe <sub>3</sub>	ClMe <sub>2</sub> Si(CH <sub>2</sub> ) <sub>6</sub> SiMe <sub>2</sub> Cl (82%) <sup>c</sup>	140°, 24 h 0.25 ml H <sub>2</sub> PtCl <sub>6</sub> <sup>e,f</sup>
3 C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> CH <sub>2</sub> SiMe <sub>3</sub>	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> CH <sub>2</sub> SiMe <sub>2</sub> Cl (81%) <sup>c</sup>	151°, 24 h 0.25 ml H <sub>2</sub> PtCl <sub>6</sub> <sup>e</sup>
4 n-C <sub>8</sub> H <sub>17</sub> SiEt <sub>3</sub>	n-C <sub>8</sub> H <sub>17</sub> SiEt <sub>2</sub> Cl (88%) <sup>c</sup>	150°, 24 h 15 mg H <sub>2</sub> PtCl <sub>6</sub>
5 n-C <sub>8</sub> H <sub>17</sub> SiEt <sub>2</sub> Me	n-C <sub>8</sub> H <sub>17</sub> SiEt <sub>2</sub> Cl (96%) <sup>c</sup>	148°, 24 h 15 mg H <sub>2</sub> PtCl <sub>6</sub>
6 C <sub>6</sub> H <sub>5</sub> SiMe <sub>3</sub>	C <sub>6</sub> H <sub>5</sub> SiMe <sub>2</sub> Cl (70%) <sup>c</sup>	155°, 24 h 15 mg H <sub>2</sub> PtCl <sub>6</sub>
7 Me <sub>3</sub> SiOSiMe <sub>3</sub>	ClMe <sub>2</sub> SiOSiMe <sub>2</sub> Cl (56%) <sup>c</sup>	150°, 24 h 15 mg H <sub>2</sub> PtCl <sub>6</sub> <sup>g</sup>
8 n-C <sub>8</sub> H <sub>17</sub> SiMe <sub>2</sub> Cl	n-C <sub>8</sub> H <sub>17</sub> SiMeCl <sub>2</sub> (14%) <sup>c</sup>	151°, 24 h 0.25 ml H <sub>2</sub> PtCl <sub>6</sub> <sup>e</sup>
9 n-C <sub>8</sub> H <sub>17</sub> SiMeCl <sub>2</sub>	no reaction	150°, 24 h 0.25 ml H <sub>2</sub> PtCl <sub>6</sub> <sup>e</sup>
10 Me <sub>3</sub> SiCl	Me <sub>2</sub> SiCl <sub>2</sub> (42%) <sup>d</sup>	156°, 24 h 15 mg H <sub>2</sub> PtCl <sub>6</sub>

<sup>a</sup>All reactions were carried out in sealed Pyrex tubes dried prior to use. The tubes were sealed at -35° and opened at -78°. <sup>b</sup>Satisfactory chemical analyses and spectral data (IR and NMR) were obtained for all silanes not previously reported in the literature. <sup>c</sup>Isolated yield. <sup>d</sup>Yield by quantitative GLPC. <sup>e</sup>Chloroplatinic acid (1.0 g) dissolved in distilled isopropanol (20.0 ml). <sup>f</sup>Fourfold excess of trichlorosilane. <sup>g</sup>Threefold excess of trichlorosilane.

exchange★. Included among these are chloroplatinic acid (both in solution and solid), platinum chloride, and dichlorodiethylene-μ,μ'-dichlorodiplatinum(II). The reaction appears to be heterogeneous since none of the catalysts seem soluble in the reaction medium. During the course of the reaction the solution and the catalyst turned black★★.

Cleavage of a silicon-carbon bond by platinum reagents has been accomplished previously<sup>2-5</sup>, but to our knowledge the reaction we are reporting is the first example wherein such catalysts have been used to effect a nearly quantitative, selective exchange of an alkyl for a chloro group on silicon★★★. The overall reaction converts relatively inert organosilanes to reactive organochlorosilanes, which are useful intermediates in synthetic organosilicon chemistry.

★Potassium tetrachloroplatinate(II) failed to effect the exchange.

★★Chloroplatinic acid was shown to retain its orange color when heated to 150° for 24 h.

★★★The redistribution and disproportionation of alkylchlorosilanes can also be selective and are well documented, although such reactions are usually catalyzed by Lewis acids and under rather vigorous conditions<sup>6</sup>.

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