METAL COMPLEX-CATALYZED REDISTRIBUTION REACTIONS OF ORGANOSILANES

IV *. REDISTRIBUTION REACTIONS OF METHYLSILOXANES CATALYZED BY TRANSITION METAL COMPLEXES

WAYNE A. GUSTAVSON, PAUL S. EPSTEIN and M.D. CURTIS *

Department of Chemistry, The University of Michigan, Ann Arbor, MI 48109 (U.S.A.)

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Summary

Redistribution reactions of a variety of hydrogen-substituted siloxanes are catalyzed by various transition metal complexes of iridium and rhodium. The products arise from breaking and remaking of Si—C, Si—H, and Si—O bonds. Siloxanes not possessing a Si—H bond are inert under the conditions studied. The most favored reaction pathway appears to scramble preferentially the groups directly attached to the silicon bearing the hydrogen atom. A new cyclo-iridiadisiloxane, \( L_2(CO)(H)Ir(SiMeROSiMeR) \) (\( L = Ph_3P; R = Me_3SiO \)) is reported. This compound exists in three isomeric forms as a consequence of the spatial arrangements of the R and Me groups on the ring.

Introduction

In an investigation of small-ring metallacycles, Curtis and Greene [1] found that cyclo-metalladisiloxanes (1) were catalysts for the disproportionation of tetramethyldisiloxane \((E'E')\) [2] into dimethylsilane and oligomeric siloxanes \((E'D,E')\) [2] (eq. 1).

A mechanism was proposed [1b and 1c] in which the strain in the four membered ring assisted the scission of an Si—O bond in 1 to give reactive, coordinated silylene and silanone intermediates. The crystal structure of 1a lent support to the argument that the Si—O bond is weakened in the metallacycle [3].

The proposed mechanism dealt specifically with the iridium complex (1a)

* For parts I—III see ref. 1.
but could be extended to some of the other complexes with minor modifications. Some consequences of the proposed mechanism are that: (i) only those siloxanes possessing the 1,3-dihydrido functionality would undergo facile redistribution since only the Si–H bond reacts readily with the low valent metal complexes, and the 1,3-arrangement is necessary to form the four-membered ring; (ii) only SiO/H exchange (see below) should occur, and (iii) the oligomers are formed sequentially, i.e., $2E'E' \rightarrow E'D'E' + Me_2SiH_2; E'E' + E'DE' \rightarrow E'D_2E' + Me_2SiH_2; E'E' + E'D_2E' \rightarrow E'D_3E' + Me_2SiH_2$, etc.

The general features of the Ir-catalyzed reaction seemed to fit all these requirements, at least at low conversions [1c]. After longer reaction times, various secondary products were observed. In order to characterize further the redistribution reaction and the effects of using different metals and different silanes, the present work was undertaken. The results show that the reaction is much more complex than originally thought and that the originally proposed metallacycle mechanism, if it is operative at all, cannot be the only mechanism whereby the groups on silicon are redistributed.

**Experimental**

All manipulations involving solutions of catalysts, reaction mixtures, etc. were done with standard Schlenk techniques under a nitrogen atmosphere. Proton and $^{13}$C [1H] NMR spectra were recorded on a Jeol JNM-PS-100 spectrometer or on a Varian T-60A. Gas chromatograms were obtained on an Antek 300, dual column instrument equipped with a thermal conductivity detector. Recording and integration of the GC spectra were accomplished with a Hewlett Packard 3380A integrator-plotter. The analytical column employed was 14'×1/8'' S.S. packed with 5% SE-30 on Chromosorb WHP 80/100. The carrier gas was He at a flow rate of 10 ml/min. Typical GC conditions are: Injector, 250°C; Detector, 300°C; temperature program: 2 min at 40°C, then increase at 4°/min to 225°C. The preparative GC column consisted of 15'×1/4'' S.S. packed with 20% SE-30 on Chromosorb A 40/60.

Mass spectra were recorded on an AEI MS902 (pure components) or on the Finnegan 4000 quadrupole spectrometer interfaced to a temperature programmable GC column, the whole being controlled by the INCOS data acquisition system [4]. When operating in the GC/MS mode, the spectra were typically
"enhanced", a procedure whereby the computer substracts out peaks which are judged to be background on the basis of their mass chromatograms. Parent ions were located either by mass chromatography (mass vs. time) or by chemical ionization techniques [4].

In cases where mass spectrometry alone would not resolve the identity of a compound, e.g., between the isomers E'DDE' and ED'D'E, the substance in question was isolated by preparative GC and analyzed by ¹H- and/or ¹³C-NMR spectroscopy. Once the identity of a compound was established, its mass spectrum was stored in the computer library. Future occurrences of the compound in mixtures could then be established by comparing its mass spectrum with the library spectrum peak for peak.

The following code will be used in the Tables to indicate the manner in which various substances were identified: 1 — comparison of GC retention times and computer matching of the mass spectra to those of authentic samples; 2 — as in method 1 plus the isolation of the product by preparative GC and analysis of its ¹H- and/or ¹³C-NMR spectra; 3 — analysis based on comparing GC retention times and MS fragmentation patterns with similar substances according to empirical rules developed in the course of this work [5] and by others [6], 4 — as in methods 1 or 3 plus substitution of Ph by Ph-d₅.

Starting siloxanes were purchased from Petrarch and were distilled prior to use. Tetramethyldisiloxane was prepared by hydrolysis of Me₂SiHCl, obtained from Dow Corning Corp. Vaska's and Wilkinson's complexes, L₂(CO)ClIr and L₃RhCl, respectively, were prepared by literature methods [7,8]. Benzene was dried over potassium/benzophenone and distilled under N₂ immediately prior to use.

**Synthesis of hydrido-1,3-[trans-bis(1,3-trimethylsiloxy)-1,3-dimethylidisiloxanediyldiy]carbonyl(bis(triphenylphosphine)iridium(III), L₂(CO)(H)Ir[SiMe(OSiMe₃)-O(SiMe(OSiMe₃)] (3)**

Vaska's complex, L₂(CO)ClIr (0.6 g, 0.8 mmol) was slurried in 10 ml of benzene. Then, 0.45 g (1.5 mmol) of 1,1,3,5,7,7,7-octamethylytetrasiloxane (ED'D'E) was added to give a cloudy, yellow solution which became clear when heated to reflux. After stirring at reflux for 1 h, the solvent was removed under vacuum to give an oil. Trituration with benzene/petroleum ether gave a white solid, m.p. 158—160°C, in 78% yield based on Ir. The 60 MHz ¹H NMR of 2 in the SiMe region consists of two broad peaks at δ 0.8 and 0.6 and a sharper peak at δ 0.2 ppm. Each of these peaks is obviously composed of overlapping unresolved peaks.

Anal. Found: C, 52.04; H, 5.48; P, 6.10; Si, 10.20; Ir, 17.70. C₄₅H₅₅IrP₂O₄Si₄ calcd.: C, 52.65; H, 5.42; P, 6.03; Si, 10.95; Ir, 18.72%. The SiOSi stretch occurs as a very strong band between 1000—1100 cm⁻¹. ν(IrH) 2080s; ν(CO) 1967s cm⁻¹.

**Redistribution reactions**

The conditions for each run are listed as footnotes in the Tables. A typical procedure is described here. Tetramethyldisiloxane (7.5 ml, 42 mmol) was added to a benzene solution (25 ml) containing 200 mg (0.26 mmol) of (Ph₃P)₂(CO)ClIr under a N₂ atmosphere. The reaction flask was equipped with
a reflux condenser, N₂ inlet, and an oil bubbler (attached at the top of the condenser and connected to the N₂ source through a T-joint). During the reaction, a static N₂ blanket was maintained in the reaction vessel. The flask was immersed in a constant temperature bath for a given time. The bulk of the solvent was then distilled off and the solvent fraction and pot residue analyzed by GC or GC/MS. This concentration step allowed for better determination of minor components.

**Kinetic runs**

In those cases where the kinetics of the redistribution reactions were determined, the reaction flask was also fitted with a 4 mm diameter side-arm tipped with a septum for GC sampling during the course of the reaction. In addition, a weighed amount of internal standard (n-heptane or n-octane) was added to the stock solutions of catalyst.

**Results and discussion**

Tables 1—4 list some of the products observed when various siloxanes containing an Si—H bond are treated with transition metal complexes. In addition to the complexes listed, several others, e.g., Rh₂(CO)₄Cl₂, Rh₂(C₂H₄)₄Cl₂, (C₂H₅)₂Rh(acac), and L₂Pt(SiMe₂OSiMe₂) (L = Ph₃P unless explicitly stated otherwise), also were found to catalyze the redistribution of tetramethyl-

### Table 1

<table>
<thead>
<tr>
<th>Product</th>
<th>% Ir</th>
<th>% Rh</th>
<th>Anal.</th>
<th>Exchange type</th>
<th>Substrate</th>
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<tr>
<td>Si₁ PhSiMe₂H</td>
<td>1.1</td>
<td>—</td>
<td>1</td>
<td>Ph/H</td>
<td>Me₂SiH₂</td>
</tr>
<tr>
<td>Si₂ E'E'</td>
<td>1.0</td>
<td>2.0</td>
<td>1</td>
<td>Ph/H</td>
<td>E'E'</td>
</tr>
<tr>
<td>Si₃ E'D'E'</td>
<td>60.4</td>
<td>8.7</td>
<td>3</td>
<td>SiO/H</td>
<td>E'E'</td>
</tr>
<tr>
<td>E'D'E'</td>
<td>—</td>
<td>5</td>
<td>1</td>
<td>SiO/Me</td>
<td>E'E'</td>
</tr>
<tr>
<td>D₃</td>
<td>0.5</td>
<td>0.8</td>
<td>1</td>
<td>SiO/H</td>
<td>E'D₂E'</td>
</tr>
<tr>
<td>D₂D'</td>
<td>0.4</td>
<td>0.8</td>
<td>3</td>
<td>SiO/Me</td>
<td>E'D₂E'</td>
</tr>
<tr>
<td>Si₄ E'D₂E'</td>
<td>21</td>
<td>13</td>
<td>2</td>
<td>SiO/H</td>
<td>E'D₂E'</td>
</tr>
<tr>
<td>E'D'D'E'</td>
<td>1.4</td>
<td>13</td>
<td>3</td>
<td>SiO/Me</td>
<td>E'D₂E'</td>
</tr>
<tr>
<td>E'D₂E'</td>
<td>—</td>
<td>1.3</td>
<td>3</td>
<td>SiO/Me</td>
<td>E'D₂E'</td>
</tr>
<tr>
<td>D₄</td>
<td>trace</td>
<td>4.1</td>
<td>1</td>
<td>SiO/Me</td>
<td>E'D₂E'</td>
</tr>
<tr>
<td>D₃D'</td>
<td>1.1</td>
<td>—</td>
<td>3</td>
<td>SiO/Me</td>
<td>E'D₂E'</td>
</tr>
<tr>
<td>Si₅ E'D₃E'</td>
<td>2.0</td>
<td>8.6</td>
<td>1</td>
<td>SiO/H</td>
<td>E'D₃E'</td>
</tr>
<tr>
<td>E'D₂D'E'</td>
<td>6.0</td>
<td>10.3</td>
<td>3</td>
<td>SiO/Me</td>
<td>E'D₃E'</td>
</tr>
<tr>
<td>E'D'D'E'</td>
<td>0.2</td>
<td>4.0</td>
<td>3</td>
<td>SiO/H</td>
<td>E'D₃E'</td>
</tr>
<tr>
<td>Si₆ E'D₄E'</td>
<td>2.0</td>
<td>11.3</td>
<td>1</td>
<td>SiO/H</td>
<td>E'D₃E'</td>
</tr>
</tbody>
</table>

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ₐ 4 ml E'E', 2 ml PhH, 120 mg L₂(CO)ClIr (140/1, E'E'/L₂(CO)ClIr), 60°C, 48 h; 39% conversion. ₆ 6 ml E'E', 4 ml PhH, 120 mg L₂RhCl (260/1, E'E'/Rh) catalyst, 60°C, 17 h; 14% conversion. ₂ Analysis code — see Experimental section. ₃ SiO/H refers to the reaction: Si(Me)H + E'E' → Si(Me)OSiMe₂H + Me₂SiH₂. ₄ SiO/Me refers to: Si(Me)(H) + E'E' → Si(H)USiMe₂H + Me₂SiH. (Si(Me)H groups are considered to be the substrates). ₅ Exchange with benzene solvent (see text). ₆ Internal exchange (see text).
Siloxanes which do not have at least one Si–H bond are inert under the conditions described in Tables 1–4. Thus, D₃, D₄, EE, and EDE remain unchanged in the presence of the transition metal complexes which cause redistribution of hydrido-siloxanes. These permethylsiloxanes are also inert in the presence of a hydrido silane and the transition metal complex. This latter observation rules out the possibility that the observed reactions occur as a result of catalysis by acidic metal “hydrides” formed in the reaction mixture.

As Table 1 shows, all the redistribution products of E'E' may be rationalized as arising from exchanges of groups adjacent to the Si–H functionality (e.g., eq. 2, 3; R' = HMeSiO).

\[
\begin{align*}
R'Me₂SiH + R'Me₂SiH & \xrightarrow{SiO/Me \text{ exchange}} R'Me₂SiR' + Me₂SiH₂ \\
\text{(E'D'E')} \\
R'Me(H)SiMe + R'Me₂SiH & \xrightarrow{SiO/Me \text{ exchange}} R'Me(H)SiR' + Me₂SiH \\
\text{(E'D'E')}
\end{align*}
\]

A second SiO/H exchange on E'DE' with E'E' (present in excess) gives the next higher oligomer according to eq. 4 (R'' = HMe₂SiOSi(Me)₂O). Continuing

\[
\begin{align*}
R''SiMe₂H + R'Me₂SiH & \xrightarrow{SiO/Me \text{ exchange}} R''SiMe₂R + Me₂SiH₂ \\
\text{(E'D₂E')}
\end{align*}
\]

in this manner, the oligomers E'DₙE' are formed sequentially via SiO/H exchange. This is by far the most favored reaction pathway for the iridium catalysis of E'E' redistribution, and is the reaction pathway in accord with the metallacycle mechanism previously proposed [1b,1c].

However, the minor products appear to arise from SiO/Me exchange as shown in eq. 3. Other minor products, e.g., the cyclic oligomers D₃ and D₄, can be accounted for on the basis of an internal SiO/H exchange as shown in eq. 5 (i.e., E'Dₙ₋₁E' → Me₂SiH₂ + Dₙ).

\[
\begin{align*}
\text{Me₂Si} & \xrightarrow{\text{(OSiMe₂)}n₋₁} \text{Me₂SiH₂} + (\text{Me₂SiO})ₙ \\
\text{(5)}
\end{align*}
\]

Neither SiO/Me exchange nor the internal SiO/H exchange of eq. 5 can be accommodated easily by the metallacycle mechanism. Although there could be two or more mechanisms operative, a faster one involving metallacycles which give the main products and slower ones accounting for the various minor products, it seems more likely that the metallacycles are not directly involved in the catalytic cycle.

With the Ir-catalyzed reactions shown in Table 1, SiO/H exchange accounts for 86% of the products shown. Only 50% of the products from the Rh-
catalyzed reaction (Table 1) can be attributed to SiO/H exchange. The Rh-catalyzed reaction also does not give the product distribution predicted on the basis of sequential oligomer formation, E'DE' → E'D2E' → E'D3E', etc. As Figure 1 shows, the oligomer E'D2E' is in greater concentration than E'DE' at all times.

The metallacycle mechanism predicts the initial concentration of E'DE' to be higher than that of E'D2E' since E'DE' is the initial, "1st turnover" product. Hence, some other mechanism must be operative, even for SiO/H exchange, with the rhodium-based catalysts. (Note: oxygen balance requires three mol of E'E' to produce one of E'D,E' no matter what the mechanism.)

The siloxanes, pentamethyldisiloxane (E'E') and hexamethyltrisiloxane (E'DE'), were subjected to redistribution conditions with L2(CO)ClIr as catalyst. E'E' does not have the second hydrogen necessary to form a four-membered metallacycle and E'DE' has been shown to give the six-membered metallacycle, 2 [1c].

\[
L_2(CO)ClIr + E'DE' \rightarrow \begin{array}{c}
\text{Ir} \\
\text{Si} \\
\text{O} \\
\text{Si} \\
\end{array} \\
(2)
\]

Fig. 1. Concentrations (M × 10⁻³) of E'E', E'DE' and E'D2E' vs. time, catalyzed by 2 × 10⁻³ M L3RhCl at 41°C.
These siloxanes undergo redistribution, although at a rate slower than that for E'E'. Figure 2 shows a graph of concentration vs. time for the redistribution of EE' and E'E'. These curves are typical for all the redistribution reactions studied to date. There is an initial rapid drop in siloxane concentration, then an abrupt break followed by a slow, zero-order reaction. The zero-order rate constants from the data in Fig. 2 are $6 \times 10^{-5}$ and $85 \times 10^{-5}$ mmol/ml/min for EE' and E'E', respectively. Dividing by the concentration of catalyst gives the turnover numbers, $1.1 \times 10^{-3}$ and $1.6 \times 10^{-2}$ mol siloxane/mol catalyst/min, for EE' and E'E', respectively. The rate for E'E' is thus about 16 times that for EE'. Whether or not the relatively modest rate increase for E'E' is due to the operation of the special, metallacyclic mechanism is questionable.

It was also observed that the following catalyst precursors all gave the same turnover numbers after the initial abrupt drop: $L_3\text{RhCl}$, $(\text{acac})\text{Rh(ethylene)}_2$ and $\text{Rh}_2(\text{CO})_4\text{Cl}_2$. This suggests that the final catalytic species are identical.

The redistribution products of pentamethyldisiloxane (EE') are shown in Table 2. The major product is ED'E which most likely comes from an exchange of trimethylsiloxy for methyl on EE' (eq. 7). The unsymmetric nature of EE'

$$2 \text{Me}_2\text{SiOSiMe}_3\text{H} \rightarrow \text{Me}_3\text{SiOSiMe(H)OSiMe}_3 + \text{Me}_3\text{SiH}$$

(eq. 7) also reveals that SiO/SiO exchanges must occur, e.g., eq. 8. The E'E' then redis-

$$2 \text{Me}_3\text{SiOSiMe}_3\text{H} \rightarrow (\text{Me}_3\text{Si})_2\text{O} + (\text{HMe}_2\text{Si})_2\text{O}$$

(eq. 8)

![Graph showing concentrations of EE' and E'E' vs. time](image-url)
TABLE 2
REDISTRIBUTION PRODUCTS OF PENTAMETHYLDISILOXANE (EE')

<table>
<thead>
<tr>
<th>Product</th>
<th>Area (%)</th>
<th>Anal.</th>
<th>Product</th>
<th>Area (%)</th>
<th>Anal.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si₂ EE</td>
<td>3.5</td>
<td></td>
<td>Si₄ ED₄E'</td>
<td>0.2</td>
<td>1</td>
</tr>
<tr>
<td>EDE</td>
<td>4.9</td>
<td>2</td>
<td>E'D₄E'</td>
<td>0.2</td>
<td>1</td>
</tr>
<tr>
<td>Si₃ E'D'E</td>
<td>0.2</td>
<td>2</td>
<td>Si₅ ED₅E</td>
<td>0.1</td>
<td>1</td>
</tr>
<tr>
<td>EDE'</td>
<td>5.7</td>
<td>1</td>
<td>E'D₅E'</td>
<td>0.2</td>
<td>1</td>
</tr>
<tr>
<td>Si₄ ED₂E</td>
<td>3.5</td>
<td>2</td>
<td>Si₆ E'D₆E</td>
<td>0.1</td>
<td>1</td>
</tr>
<tr>
<td>EDD'E</td>
<td>6.4</td>
<td>2</td>
<td>E'D₆E'</td>
<td>0.1</td>
<td>1</td>
</tr>
<tr>
<td>E'D₂E'</td>
<td>6.4</td>
<td>2</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>E'D'D'E'</td>
<td>1.7</td>
<td>3</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Si₅ ED₃E</td>
<td>0.7</td>
<td>1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ED₂D'E</td>
<td>0.9</td>
<td>3</td>
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<td></td>
</tr>
<tr>
<td>ED₃E'</td>
<td>0.6</td>
<td>1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>E'D₃E'</td>
<td>0.1</td>
<td>1</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* 39 mmol EE' and 0.773 mmol L₂(CO)ClIr in 15.0 ml C₆H₆ for 116 h at 70°C; 16% conversion. b GC area percents of products with >2 silicon per molecule. Some Me₃SiH and EE also detected. c Analysis code, (see Experimental section). d Phenyl groups from solvent, (see text).

Table 3 presents the redistribution products of E'DE'. One of the major products, E'D₂E', is again most probably formed as a result of the SiO/SiO exchange shown in the Table. The other major product is the cyclic tetramer, D₃D'. If this cyclic forms from an internal exchange (cf. eq. 5), then its precursor is E'D'D'D'E', the expected first turnover product resulting from the SiO/Me exchange shown in Table 3. If this scheme is correct, then the E'D'D'D'E' must cyclize nearly as fast as it is formed since its concentration is extremely low for a 1st turnover product.

ED'D'E reacts with L₂(CO)ClIr to give a mixture of the metallacycles 3a–3c (R = Me₃SiO) [9]. The overall composition is well established by elemental analysis. However, the ¹H NMR in the Si-Me region consists of a set of overlapping peaks in three main "bunches" at δ 0.8, 0.6 and 0.2. Five peaks and two shoulders are distinguishable. The mixture of isomers 3–5 should give a total of eight methyl environments.

If the redistribution reaction of ED'D'E were to proceed via the previously proposed metallacycle mechanism, then the primary reaction products would
be given by eq. 9 \((R = \text{Me}_3\text{SiO})\). The oligomeric siloxanes should have pendant
\((n + 1)\text{ED'}\text{D'}\text{E} \rightarrow \text{ED'}(-\text{T}--)_{n}\text{D'}\text{E} + n \text{RMeSiH}_2\)
\(\text{(9)}\)

\(\text{Me}_3\text{SiO} \text{ groups along the polymer backbone. The RMeSiH}_2 \text{ should disproportionate very rapidly to give products, e.g., MeSiH}_{3(\text{g})} \text{ and ED'E via R/H (R = Me}_3\text{SiO) exchanges [9]. However, the products listed in Table 4 are best rationalized by assuming that both SiO bonds adjacent to the hydrogen-bearing silicon are labilized, not just the central Si-O bond as would be the case if a metallacycle were necessary to cause labilization.}

\[
\begin{align*}
\text{Me}_3\text{SiO} & \quad \text{Si} \quad \text{O} \quad \text{SiOSiMe}_3 \\
\end{align*}
\]

TABLE 4

<table>
<thead>
<tr>
<th>Product (^{a,b})</th>
<th>Area (%) (^c)</th>
<th>Empirical formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>\text{ED'E}</td>
<td>13.9</td>
<td>\text{Me}_7\text{Si}_3\text{HO}_2</td>
</tr>
<tr>
<td>\text{E}_3\text{T}</td>
<td>3.4</td>
<td>\text{Me}_{16}\text{Si}_4\text{O}_3</td>
</tr>
<tr>
<td>\text{E}_2\text{T'D'E}</td>
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<td>\text{Me}_{10}\text{Si}_5\text{H}_2\text{O}_4</td>
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<tr>
<td>\text{E}_2\text{T'D'E}</td>
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<td>\text{Me}_{11}\text{Si}_5\text{HO}_4</td>
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<tr>
<td>\text{ET(D'E)_2}</td>
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</tr>
<tr>
<td>\text{ET(D'E)_2}</td>
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<td>\text{Me}_{14}\text{Si}_6\text{O}_5</td>
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<tr>
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<td>\text{ET(D'E)(D'E)}_2</td>
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<td>\text{Me}_{14}\text{Si}_7\text{H}_2\text{O}_6</td>
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<tr>
<td>\text{ET(D'E)(D'E)}_2</td>
<td>3.9</td>
<td>\text{Me}_{15}\text{Si}_7\text{HO}_6</td>
</tr>
<tr>
<td>\text{(ED'E)_2 (E')}</td>
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<td>\text{Me}_{16}\text{Si}_8\text{H}_2\text{O}_7</td>
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<tr>
<td>\text{ET(T'E)_2}</td>
<td>3.9</td>
<td>\text{Me}_{17}\text{Si}_9\text{H}_3\text{O}_8</td>
</tr>
</tbody>
</table>

\(^a 2.0 \text{ M ED'E}', 0.01 \text{ M } \text{L}_2(\text{CO})\text{ClIr in benzene; 60°C; 90 h; 12% conversion.} \quad \text{Structure of products with more than 4 Si atoms assigned only on basis of assumed mechanism of formation (see text).} \quad \text{GC area (%) of products only. Minor products (<1%) omitted.} \)
In other words, ED'I, upon its interaction with the catalyst, supplies E, ED', and ED' groups for exchange with Si-O, Si-Me, and Si-H bonds. The predicted "1st turnover" products are then given by the following equations:

SiO/SiO exchanges:

\[
ED'_I \rightarrow [E, D'_I, ED'] \rightarrow ED'E + ED'_I + ED'I
\]  
(10)

SiO/H exchanges:

\[
ED'_I \rightarrow [E, D'_I, ED'] \rightarrow ET(D'E)_2
\]  
(11)

SiO/Me exchanges:

\[
ED'_I \rightarrow [E, D'_I, ED'] \rightarrow ET(D'E)_2 + ET(D'E)_2
\]  
(12)

Of the predicted possibilities, ED'E is definitely observed; and Si₅H, Si₅H₂, two Si₆H₂ isomers, and an Si₆H₃ isomer are observed. These may possibly correspond to the species in eq. 10-12. The remaining species can all be rationalized as "2nd turnover" products resulting from E/H, ED'/H, ED'I/H, etc. exchanges on the "1st turnover" products. It is interesting to note that the Si₅H₂ isomer of possible structure, ED'[T(E)]₂D'E, is a "2nd turnover" product according to this scheme, but has the second highest concentration of any product. This same phenomenon occurs in the Rh-catalyzed redistribution of E'E' wherein the "2nd turnover" product, E'D₂E' has a higher concentration than the supposed "1st turnover" product, E'DE' (see Fig. 1). In any event, the metal complex catalyzed redistribution of ED'E leads to a very complex mixture, the composition of which is consistent with the notion that Si-O and Si-Me bonds adjacent to Si-H bonds are labilized and undergo exchange reactions.

Finally, we note that the metal species which are formed in the presence of Si-H bonds are sufficiently active to activate the C-H bond of benzene to substitution by Si [1a]. As shown in Tables 1 and 2, various phenyl substituted siloxanes and silanes are produced along with the rearrangement products. That the benzene solvent is the source of these phenyl groups in the case of iridium catalysts was demonstrated by using C₆D₆ as the solvent. The resulting phenyl-containing products are d₅-substituted and their fragmentation patterns are entirely consistent with their being d₅-phenyl groups [5].
Conclusion

Siloxanes having at least one Si–H bond undergo redistribution reactions in the presence of certain transition metal complexes, especially those of Pt, Pd, Ir and Rh. The observed products are formed as a result of scrambling all the groups attached to the silicon bearing the hydrogen atom; and, to a much lesser extent, as a result of more common SiO/SiO exchanges as observed with acid or base catalyzed rearrangements [1b,10]. It appears that with the transition metal catalysts, SiO/Me and SiO/H exchanges are faster than SiO/SiO exchanges, so that these redistributions complement the classical acid or base catalyzed redistributions. Synthetic useful rates and selectivities have been achieved recently by supporting the iridium complexes on high surface area oxides [11].

The nature of the metal-silyl species involved in the catalytic cycle is unclear, although several possibilities have been discussed in some detail [1b]. Likely intermediates are mono- and di-nuclear silylene complexes, M=SiR₂ and M–SiR₂–M, respectively, and complexed silylones. The remarkable stability of appropriately substituted silylenes has been demonstrated recently [12], and silylones are commonly postulated as intermediates [13].

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References


2 The abbreviated notation for siloxanes used here is as follows: E (end group) = MegSiO₂, D (difunctional) = MegSiO₂, T (trifunctional) = MegSiO₃. A primed letter indicates a substitution of hydrogen for methyl (e.g., D' = HMeSiO₂), and a superscript "P" indicates substitution of phenyl for methyl (e.g., EP = PhMe₂SiO₂). For example: Me₃SiOSiMe₂H = EE'; PhMe₂SiOSiMe₂OSiMe₂H = EPDE'; (Me₃SiO)₃SiH = E₃T'.


5 A detailed account of the identification of organosiloxanes by combined electron impact — (EIMS) and chemical ionization mass spectrometry (CIMS) will be given elsewhere: M.D. Curtis and P.S. Epstein, to be published.


9 The disiloxane, (HBzMeSi)₂O (Bz = benzyl), also gives a mixture of cis- and trans-metallacycles with L₂PtCl₂: L.G. Bell, W.A. Gustavson and M.D. Curtis, submitted for publication.


11 W.A. Gustavson and M.D. Curtis, to be submitted.
