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REDISTRIBUTION REACTIONS OF METHYLSILOXANES CATALYZED  
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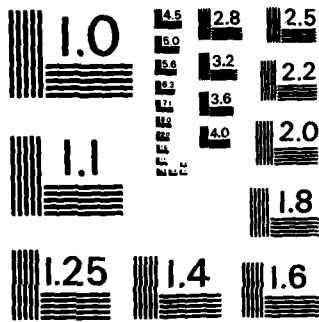
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Siloxanes containing at least one Si-H bond undergo a redistri- bution reaction catalyzed by transition metal complexes of Ir, Rh, and Pt. A new metalla-cyclodisiloxane of Ir is described.		

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Redistribution Reactions of Methylsiloxanes  
Catalyzed by Transition Metal Complexes

by

W.A. Gustavson, P.S. Epstein, and M.D. Curtis

Prepared for publication in the  
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REDISTRIBUTION REACTIONS OF METHYLSILOXANES CATALYZED BY TRANSITION METAL COMPLEXES.<sup>1</sup>

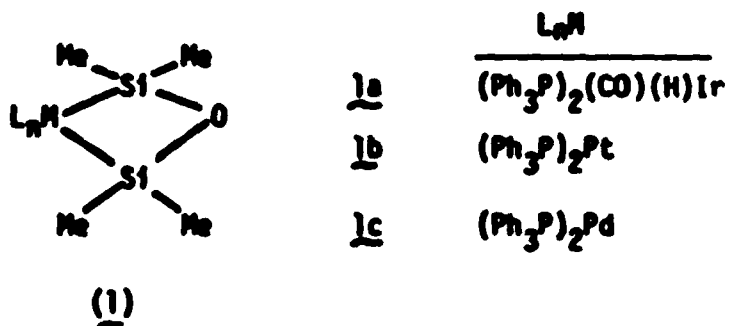
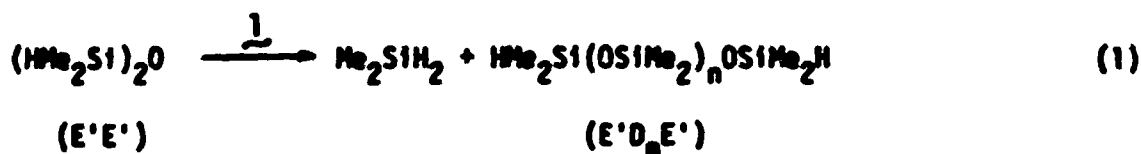
Wayne A. Gustavson, Paul S. Epstein, and M. D. Curtis,\* Department of Chemistry, The University of Michigan, Ann Arbor, MI 48109.

ABSTRACT

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 preferentially scramble the groups directly attached to the silicon bearing the hydrogen atom. A new cyclo-iridiasiloxane,  $L_2^-(CO)(H) - \text{Ir}(\text{SiMeOSiMeR})$  ( $L = \text{Ph}_3\text{P}$ ,  $R = \text{Me}_3\text{SiO}$ ) 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<sup>1</sup> found that cyclo-metalladisiloxanes, 1, were catalysts for the disproportionation of tetramethyldisiloxane (E'E')<sup>2</sup> into dimethylsilane and oligomeric siloxanes (E'D<sub>n</sub>E')<sup>2</sup> (eq. 1).



A mechanism was proposed<sup>1b,c</sup> 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.<sup>3</sup>

The proposed mechanism dealt specifically with the iridium complex, 1a, but could be extended to some of the other complexes with minor modifications. Some consequences of the proposed mechanism are that: (1) 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; (2) only SiO/H exchange (see below) should occur, and (3) the oligomers are formed sequentially, i.e.,  $2E'E' + E'DE' + Me_2SiH_2$ ;  $E'E' + E'DE' \rightarrow E'D_2E' + Me_2SiH_2$ ;  $E'E' + E'D_2E' \rightarrow E'D_3E' + Me_2SiH_2$ , etc.

The general features of the Ir-catalyzed reaction seemed to fit all these requirements, at least at low conversions.<sup>1c</sup> After longer reaction times, various secondary products were observed. In order to further characterize 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' x 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°; Detector, 300°; temperature program: 2 min. at 40°, then increase at 4°/min. to 225°. The preparative GC column consisted of 15' x 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.<sup>4</sup> When operating in the GC/MS mode, the spectra were typically "enhanced", a procedure whereby the computer subtracts 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.<sup>4</sup>

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 <sup>1</sup>H- and/or <sup>13</sup>C-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 <sup>1</sup>H- and/or <sup>13</sup>C-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<sup>5</sup> and by others<sup>6</sup>, 4 - as in methods 1 or 3 plus substitution of Ph by Ph-d<sub>5</sub>.

Starting siloxanes were purchased from Petrarch and were distilled prior to use. Tetramethyldisiloxane was prepared by hydrolysis of Me<sub>2</sub>SiHCl, obtained from Dow Corning Corp. Vaska's and Wilkinson's complexes, L<sub>2</sub>(CO)ClIr and L<sub>2</sub>RhCl, respectively, were prepared by literature methods.<sup>7,8</sup> Benzene

was dried over potassium/benzophenone and distilled under  $N_2$  immediately prior to use.

Synthesis of Hydrido -1,3-(trans-bis(1,3-trimethylsiloxy)-1,3-dimethyldisiloxanedyl)carbonylbis(triphenylphosphine)iridium(III),  $L_2(CO)(H)Ir[SiMe(OSiMe_3)_2OSiMe(OSiMe_3)]_2$ . Vaska's complex,  $L_2(CO)ClIr$  (0.6g, 0.8 mmole) was stirred in 10 ml of benzene. Then, 0.45 g (1.5 mmole) of 1,1,1,3,5,7,7,7-octamethyltetrasiloxane (ED'O'E) was added to give a cloudy, yellow solution which became clear when heated to reflux. After stirring at reflux for 1 hr., the solvent was removed under vacuum to give an oil. Trituration with benzene/pet. ether gave a white solid, m.p. 158-160°, in 78% yield based on Ir. The 60 MHz  $^1H$ -NMR of 2 in the  $SiMe_3$  region consists of two broad peaks at 60.8 and 0.6 and a sharper peak at 60.2. Each of these peaks is obviously composed of overlapping unresolved peaks.

Anal.: Calcd. for  $C_{66}H_{56}IrP_2O_4Si_4$ : C, 52.65; H, 5.42; P, 6.03; Si, 10.95; Ir, 18.72. Found: C, 52.04; H, 5.48; P, 6.10; Si, 10.20; Ir, 17.70. The SiOSi stretch occurs as a v. strong band between 1000 - 1100  $cm^{-1}$ .  $\nu_{IrH}$ : 2080(s);  $\nu_{CO}$ : 1967(s)  $cm^{-1}$ .

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 mmole) was added to a benzene solution (25 ml) containing 200 mg (0.26 mmole) of  $(Ph_3P)_2(CO)ClIr$  under a  $N_2$ -atmosphere. The reaction flask was equipped with a reflux condenser,  $N_2$  inlet, and an oil bubbler (attached at the top of the condenser and connected to the  $N_2$  source through a T-joint). During the reaction, a static  $N_2$  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.

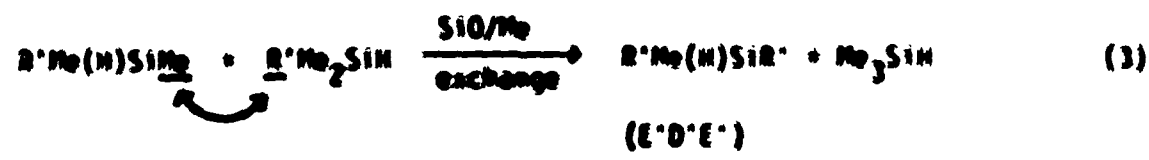
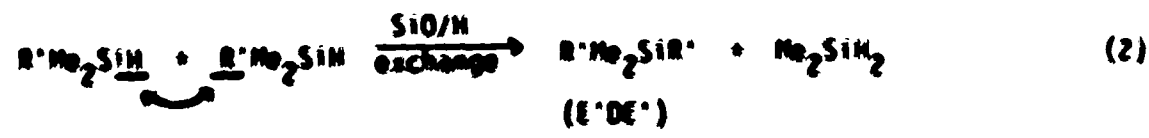
Kinetic Runs. In those cases where the kinetics of the redistribution reactions were determined, the reaction flask was also fitted with a 4 mm diameter side-arm tipped with a septum for GC sampling during the course of the reaction. In addition, a weighed amount of internal standard (n-heptane or n-octane)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

## RESULTS AND DISCUSSION

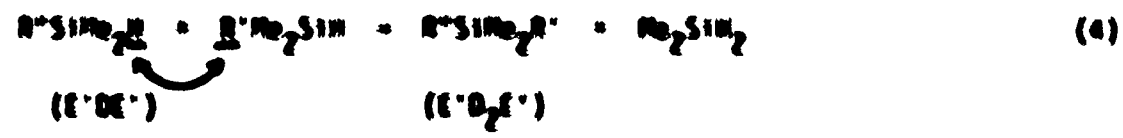
Tables I-IV list some of the products observed when various siloxanes containing an Si-H bond are treated with transition metal complexes. In addition to the complexes listed, several others, e.g.,  $\text{Rh}_2(\text{CO})_4\text{Cl}_2$ ,  $\text{Rh}_2(\text{C}_2\text{H}_4)_4\text{Cl}_2$ ,  $(\text{C}_2\text{H}_4)_2\text{Rh}(\text{acac})$ , and  $\text{L}_2\text{Pt}(\text{SiMe}_2\text{OSiMe}_2)$  (L =  $\text{Ph}_3\text{P}$  unless explicitly stated otherwise), also were found to catalyze the redistribution of tetramethyldisiloxane, E'E'. However, the products are essentially the same as those listed in Table I.

Siloxanes which do not have at least one Si-H bond are inert under the conditions described in Tables I-IV. Thus,  $\text{D}_3$ ,  $\text{D}_4$ , 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 I 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., eqs. 2,3; R' = HMeSiO-).



A second SiO/M exchange on E'DE' with E'E' (present in excess) gives the next higher oligomer according to eq. 4 (R' = HMe<sub>2</sub>SiOSi(Me)<sub>2</sub>O-). Continuing

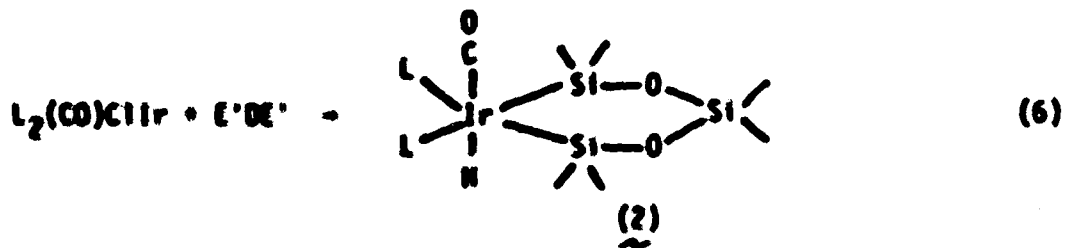


in this manner, the oligomers E'D<sub>n</sub>E' are formed sequentially via SiO/M exchange. This is by far the most favored reaction pathway for the iridium catalysis of E'E' redistribution, and is the reaction pathway in accord with the metal-cycle mechanism previously proposed.<sup>1b,c</sup>



The metallacycle mechanism predicts the initial concentration of E'DE' to be higher than that of E'D<sub>2</sub>E' 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 moles of E'E' to produce one of E'D<sub>2</sub>E' no matter what the mechanism.)

The siloxanes, pentamethyldisiloxane (EE') and hexamethyltrisiloxane (E'E'), were subjected to redistribution conditions with L<sub>2</sub>(CO)ClIr as catalyst. EE' 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

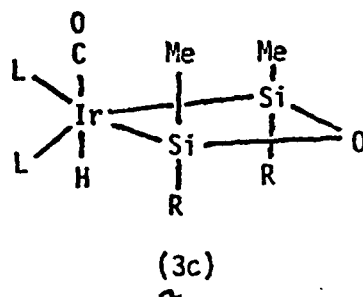
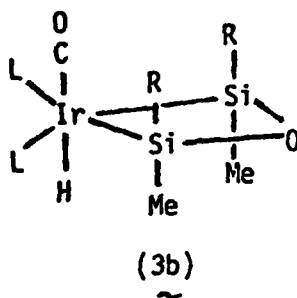
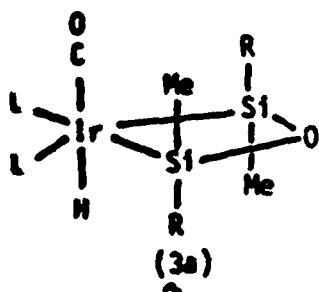


These siloxanes undergo redistribution, although at a rate slower than that for E'E'. Figure 2 shows a graph of concentration vs. time for the redistribution of EE' and E'E'. These curves are typical for all the redistribution reactions studied to date. There is an initial rapid drop in siloxane concentration, then an abrupt break followed by a slow, zero-order reaction. The zero-order rate constants from the data in Figure 2 are  $6 \times 10^{-5}$  and  $85 \times 10^{-5}$  mmole/ml/min for EE' and E'E', respectively. Dividing by the concentration of catalyst gives the turnover numbers,  $1.1 \times 10^{-3}$  and  $1.6 \times 10^{-2}$  moles siloxane/mole



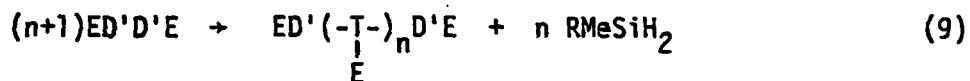
Table III presents the redistribution products of E'DE'. One of the major products, E'D<sub>2</sub>E', is again most probably formed as a result of the SiO/SiO exchange shown in the Table. The other major product is the cyclic tetramer, D<sub>3</sub>D'. If this cyclic forms from an internal exchange (cf. eq. 5), then its precursor is E'DD'DE', the expected first turnover product resulting from the SiO/Me exchange shown in the Table. If this scheme is correct, then the E'DD'DE' must cyclize nearly as fast as it is formed since its concentration is extremely low for a 1st turnover product.

E'D'E reacts with L<sub>2</sub>(CO)ClIr to give a mixture of the metallacycles 3a-3c (R = Me<sub>3</sub>SiO).<sup>9</sup> The overall composition is well established by elemental

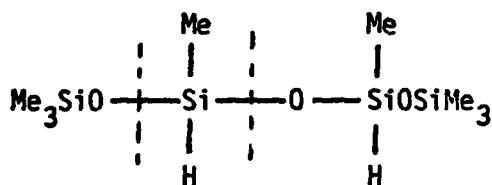


analysis. However, the <sup>1</sup>H-NMR in the Si-Me region consists of a set of overlapping peaks in three main "bunches" at δ 0.8, 0.6 and 0.2. Five peaks and two shoulders are distinguishable. The mixture of isomers 3-5 should give a total of eight methyl environments.

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 = Me<sub>3</sub>SiO). The oligomeric siloxanes should

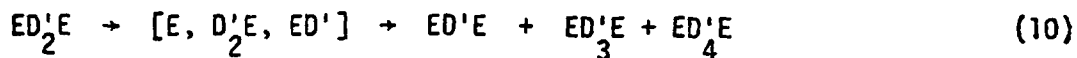


have pendant Me<sub>3</sub>SiO groups along the polymer backbone. The RMeSiH<sub>2</sub> should disproportionate very rapidly to give products, e.g., MeSiH<sub>3</sub>(g) and ED'E via R/H (R = Me<sub>3</sub>SiO) exchanges.<sup>9</sup> However, the products listed in Table IV are best rationalized by 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.

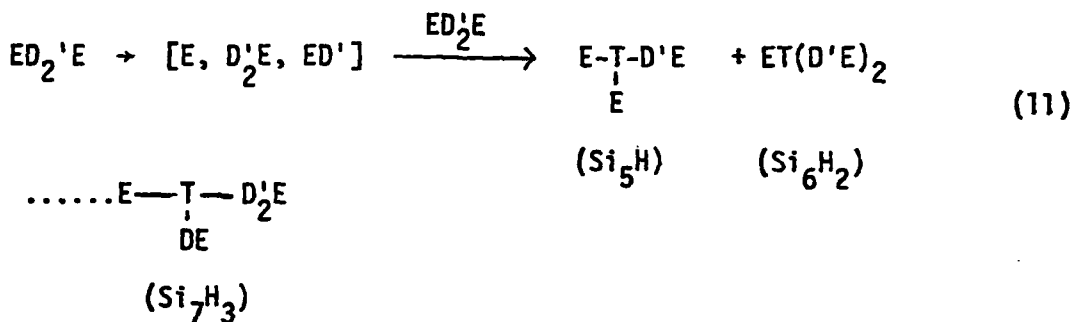


In other words, ED<sub>2</sub>E, upon its interaction with the catalyst, supplies E, ED<sub>2</sub>, and ED' groups for exchange with SiO, Si-Me, and Si-H bonds. The predicted "1st turnover" products are then given by the following equations:

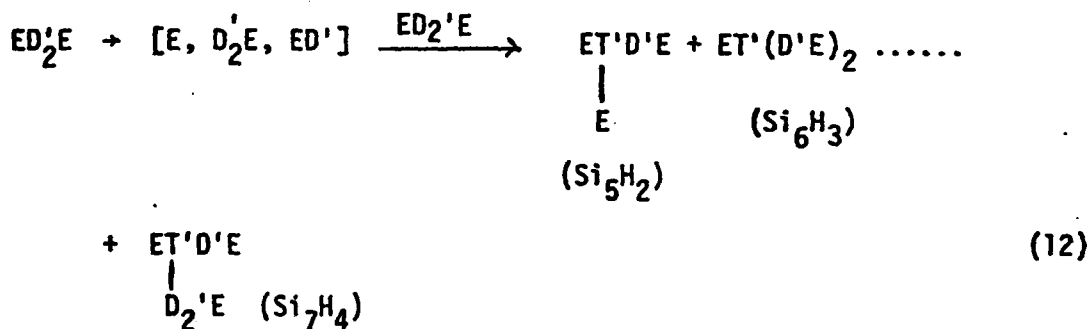
SiO/SiO exchanges:



SiO/H exchanges:



SiO/Me exchanges:



Of the predicted possibilities, ED'E is definitely observed; and Si<sub>5</sub>H, Si<sub>5</sub>H<sub>2</sub>, two Si<sub>6</sub>H<sub>2</sub> isomers, and an Si<sub>7</sub>H<sub>3</sub> isomer are observed. These may possibly correspond to the underlined species in eq. 10-12. The remaining species can all be rationalized as "2nd turnover" products resulting from E/H, ED'/H, ED<sub>2</sub>'/H, etc. exchanges on the "1st turnover" products. It is interesting to note

that the  $\text{Si}_8\text{H}_2$  isomer of possible structure,  $\text{ED}'[\text{T}(\text{E})]_2\text{D}'\text{E}$ , 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  $\text{E}'\text{E}'$  wherein the "2nd turnover" product,  $\text{E}'\text{D}_2\text{E}'$  has a higher concentration than the supposed "1st turnover" product,  $\text{E}'\text{DE}'$  (see Fig. 1). In any event, the metal complex catalyzed redistribution of  $\text{ED}'_2\text{E}$  leads to a very complex mixture, the composition of which is consistent with the notion that  $\text{SiO}$  and  $\text{SiMe}$  bonds adjacent to  $\text{Si-H}$  bonds are labilized and undergo exchange reactions.

Finally, we note that the metal species which are formed in the presence of  $\text{Si-H}$  bonds are sufficiently active to activate the  $\text{C-H}$  bond of benzene to substitution by  $\text{Si}$ .<sup>10</sup> As shown in Tables I and II, 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  $\text{C}_6\text{D}_6$  as the solvent. The resulting phenyl-containing products are  $\text{d}_5$ -substituted and their fragmentation patterns are entirely consistent with their being  $\text{d}_5$ -phenyl groups.<sup>5</sup>

#### SUMMARY

Siloxanes having at least one  $\text{Si-H}$  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  $\text{SiO/SiO}$  exchanges as observed

with acid or base catalyzed rearrangements.<sup>1b,11</sup> It appears that with the transition metal catalysts, SiO/Me and SiO/H exchanges are faster than SiO/SiO exchanges, so that these redistributions compliment the classical acid or base catalyzed redistributions. Synthetically useful rates and selectivities have been achieved recently by supporting the iridium complexes on high surface area oxides.<sup>12</sup>

The nature of the metal-silyl species involved in the catalytic cycle is unclear, although several possibilities have been discussed in some detail.<sup>1b</sup> Likely intermediates are mono- and dinuclear silylene complexes and complexed silanones. The remarkable stability of appropriately substituted silylenes has been demonstrated recently,<sup>13</sup> and silanones are commonly postulated as intermediates.<sup>14</sup>

#### ACKNOWLEDGEMENTS

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2. The abbreviated notation for silicones used here is as follows:  
E (end group) =  $\text{Me}_3\text{SiO}_{1/2}$ , D (difunctional) =  $\text{Me}_2\text{SiO}_{2/2}$ ; T (trifunctional) =  $\text{MeSiO}_{3/2}$ . A primed letter indicates a substitution of hydrogen for methyl (i.e.,  $\text{D}' = \text{HMeSiO}_{2/2}$ ), and a superscript "P" indicates substitution of phenyl for methyl (e.g.,  $\text{E}^{\text{P}} = \text{PhMe}_2\text{SiO}_{1/2}$ ). For example:  
 $\text{Me}_3\text{SiOSiMe}_2\text{H} = \text{EE}'$ ;  $\text{PhMe}_2\text{SiOSiMe}_2\text{OSiMe}_2\text{H} = \text{E}^{\text{P}}\text{DE}'$ ;  $(\text{Me}_3\text{SiO})_3\text{SiH} = \text{E}_3\text{T}'$ , etc.
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TABLE I. REDISTRIBUTION PRODUCTS OF TETRAMETHYLDISTOXANE (E'E') CATALYZED BY L<sub>2</sub>(CO)<sub>2</sub>FIR AND L<sub>2</sub>PHCl

Product	$\bar{X}(I)^a$	$\bar{X}(M)^b$	Anal.	exchange type	substrate
S <sub>11</sub> PhSiMe <sub>2</sub> H	1.1	-	1	Ph/H <sup>c</sup>	Me <sub>2</sub> SiH <sub>2</sub>
S <sub>12</sub> E <sup>p</sup> E'	1.0	2.0	1	Ph/H <sup>c</sup>	E'E'
S <sub>13</sub> E'DE'	60.4	8.7	3	SiO/H	E'E'
E'D'E'	-	5	1	SiO/Me	E'E'
D <sub>3</sub>	0.5	0.8	1	SiO/H <sup>f</sup>	E'D <sub>2</sub> E'
D <sub>2</sub> <sup>d</sup>	0.4	0.8	3	SiO/Me <sup>f</sup>	E'D <sub>2</sub> E'
S <sub>14</sub> E'D <sub>2</sub> E'	21	13	2	SiO/H	E'DE'
E'DD'E'	1.4	13	3	SiO/Me	E'DE'
E'D <sub>2</sub> E'		1.3	3	SiO/Me	E'DE'
D <sub>4</sub>	trace	4.1	1	SiO/H <sup>f</sup>	E'D <sub>2</sub> E'
D <sub>3</sub> <sup>d</sup>	1.1	-	3	SiO/Me <sup>f</sup>	E'D <sub>2</sub> E'
S <sub>15</sub> E'D <sub>2</sub> E'	2.0	8.6	1	SiO/H	E'D <sub>2</sub> E'
E'D <sub>2</sub> D'E'	6.0	10.3	3	SiO/Me	E'D <sub>2</sub> E'
E'DD'DE'	0.2	4.0	3	SiO/H	EDD'E'
S <sub>16</sub> E'D <sub>4</sub> E'	2.0	11.3	1	SiO/H	E'D <sub>2</sub> E'

Table 1 (continued)

footnotes

- a) 4 mL E'E', 2 mL PhH, 120 mg  $L_2(CO)ClIr$  (140:1 E'E':  $L_2(CO)ClIr$ ), 60°, 48 hr. (39% conversion).
- b) 6 mL E'E', 4 mL PhH, 120 mg  $L_2PhCl$  (260: 1 E'E':Rh) catalyst, 60°, 17 hr. (4% conversion).
- c) Analysis code - see experimental section.
- d)  $SiO/H$  refers to the reaction:  $Si(Ph)H + E'E' \rightarrow Si(Ph)OSiPh_2H + Ph_2SiH_2$ ;  $SiO/Ph$  refers to:  
 $Si(Ph)(H) + E'E' \rightarrow Si(H)OSiPh_2H + Ph_2SiH_2$ . The underlined species are considered to be the substrates.
- e) Exchange with benzene solvent (see text).
- f) Internal exchange (see text).

TABLE 11. Redistribution Products of Pentamethylsiloxane (EE').<sup>a</sup>

Product	Area % <sup>b</sup>	Anal. C	Product	Area % <sup>b</sup>	Anal. C
S12	3.5		S16	0.2	1
EE	4.9	2	ED <sub>4</sub> E		
ED <sub>2</sub> E	60.2	2	ED <sub>3</sub> E'	0.2	1
ED'E	5.7	1	E'D <sub>4</sub> E'	0.1	1
ED <sub>2</sub> E'					
S14	3.5	2	S17	0.1	1
ED <sub>2</sub> E	6.4	2	ED <sub>3</sub> E		
ED'D'E	6.4	2	ED <sub>3</sub> E'	0.1	3
E'D <sub>2</sub> E'			E'D <sub>3</sub> E'	0.1	1
E'DD'E'	1.7	3			
S15	0.7	1	<u>Phenylsiloxanes<sup>d</sup></u>		
ED <sub>3</sub> E	0.9	3	E'E	2.1	4
ED <sub>2</sub> D'E	0.6	1	E'DE	1.5	4
ED <sub>3</sub> E'	0.1	1	E'D <sub>2</sub> E	0.8	4

a) 30 mmole EE' and 0.773 mmoles L<sub>2</sub>(CO)ClIr in 15.0 mL C<sub>6</sub>H<sub>6</sub> for 116 hr. at 70°, 10% conversion.

b) GC area percents of products with ≥2 silicon per molecule. Some Me<sub>2</sub>SiH and EE also detected.

c) Analysis code - see experimental section.

d) Phenyl groups from solvent - see text.

TABLE III. Redistribution Products of Hexamethyltrisiloxane (E'DE').

Products <sup>a</sup>	Area % <sup>b</sup>	Formation <sup>c</sup>
Me <sub>3</sub> SiH	0.1	—
E'DD'E	0.8	E'/Me on E'DE'
D <sub>3</sub> D'	48.3	Cyclization of E'DD'DE' (?)
E'D <sub>2</sub> E'	38.1	E'D/E' on E'DE'
E'DD'DE' <sup>d</sup>	1.0	E'D/Me on E'DE'
E'D <sub>3</sub> E'	6.1	E'D/H on E'DE'
E'D <sub>4</sub> E'	5.3	E'D/H on E'D <sub>2</sub> E'

a) 2.04 M E'DE' in benzene; .01 M L<sub>2</sub>(CO)Cl/r, 80°, 46 hr. (6% conversion).

b) GC area percents of products only.

c) Probable mode of formation.

d) Structure assigned on basis of expected exchange mode.

TABLE IV. Redistribution Products of Octamethyltetrasiloxane, ED'D'E

Product <sup>a,b</sup>	Area % <sup>c</sup>	empirical formula
ED'E	13.9	$\text{M}_7\text{Si}_3\text{H}_2\text{O}_2$
$\text{L}_3\text{T}$	3.4	$\text{M}_{10}\text{Si}_4\text{O}_3$
$\text{L}_2\text{T}'\text{D}'\text{E}$	1.9	$\text{M}_{10}\text{Si}_5\text{H}_2\text{O}_4$
$\text{L}_2\text{TD}'\text{E}$	7.5	$\text{M}_{11}\text{Si}_5\text{H}_2\text{O}_4$
$\text{ET}(\text{D}'\text{E})_2$	5.0	$\text{M}_{12}\text{Si}_6\text{H}_2\text{O}_5$
$\text{L}_2\text{TD}'_2\text{E}$	1.0	$\text{M}_{12}\text{Si}_6\text{H}_2\text{O}_5$
$\text{L}_2\text{TTE}_2$	1.0	$\text{M}_{14}\text{Si}_6\text{O}_5$
<del><math>\text{ET}(\text{D}'\text{E})(\text{D}'\text{E})</math></del>	<del>2.3</del>	<del><math>\text{M}_{13}\text{Si}_7\text{H}_2\text{O}_6</math></del>
$(\text{E}')_2\text{OE}_2$	1.5	$\text{M}_{14}\text{Si}_7\text{H}_2\text{O}_6$
$\text{L}_2\text{TD}'\text{TE}_2$	3.9	$\text{M}_{15}\text{Si}_7\text{H}_2\text{O}_6$
$(\text{ED}'\text{T} - )_2$	13.1	$\text{M}_{16}\text{Si}_8\text{H}_2\text{O}_7$
--	3.9	$\text{M}_{17}\text{Si}_9\text{H}_2\text{O}_8$

a) 2.0 M ED'D'E, .01M  $\text{L}_2(\text{CO})\text{ClIr}$  in benzene; 60°; 90 hr.; 12% conversion.

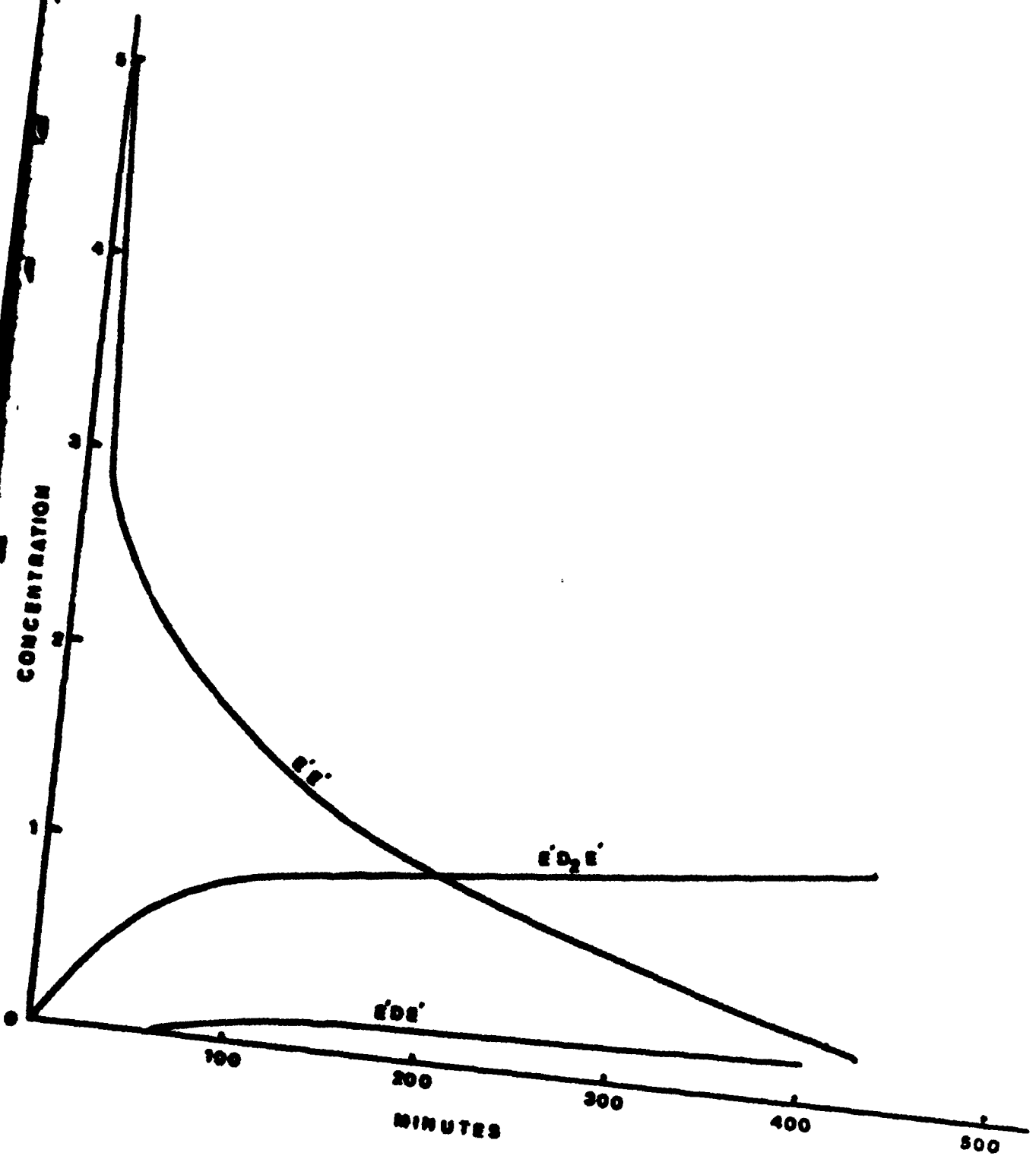
b) Structure of products with more than 4 Si-atoms assigned only on basis of assumed mechanism of formation - see text.

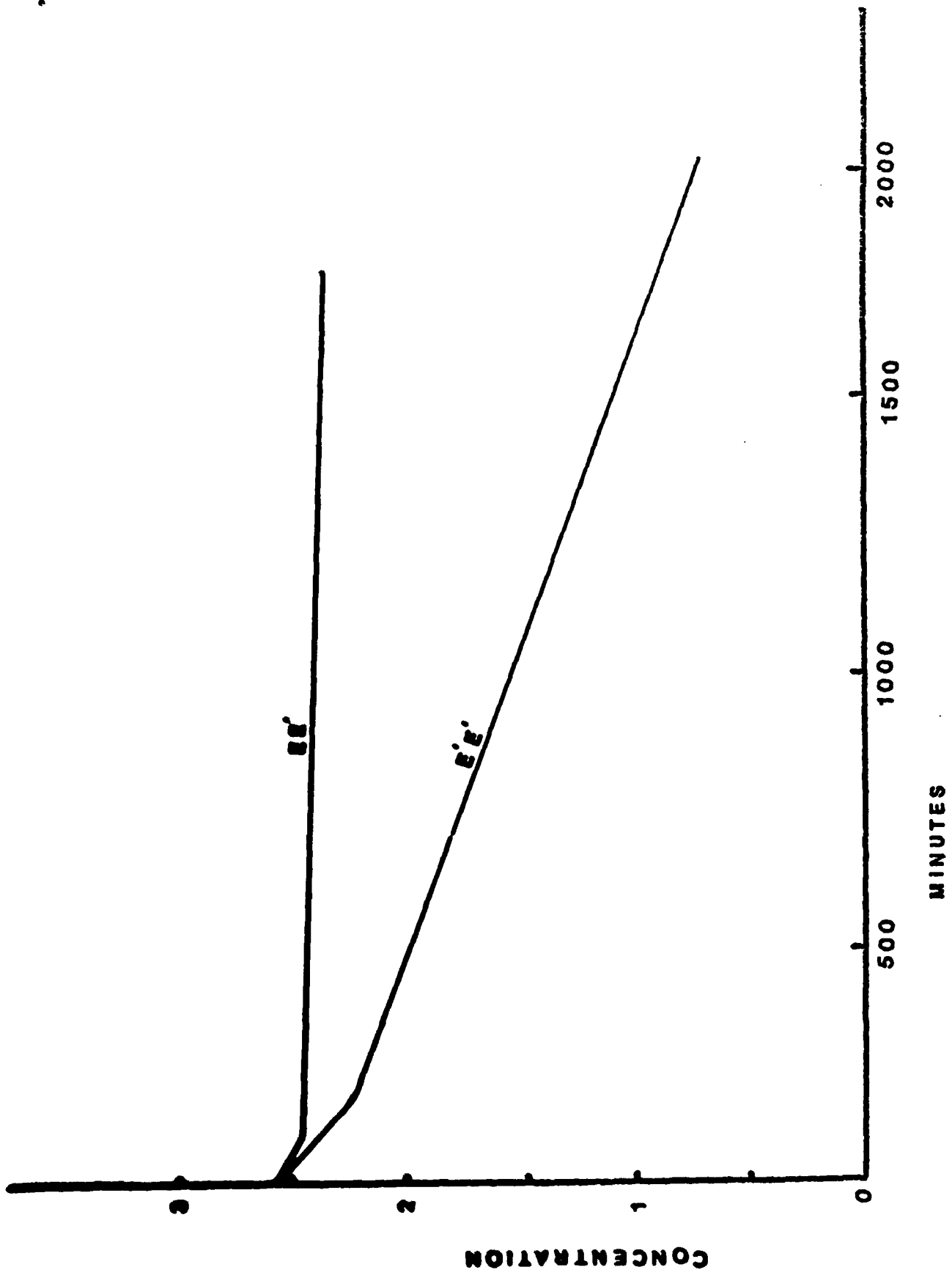
c) GC area % of products only. Minor products (<1 %) omitted.

CAPTIONS TO THE FIGURES

Figure 1. Concentrations ( $M \times 10^3$ ) of  $E^*E^*$ ,  $E^*DE^*$  and  $E^*D_2E^*$  vs. time, catalyzed by  $2 \times 10^{-3}M L_2RuCl$  at  $41^\circ$ .

Figure 2. Concentrations (moles/l) of  $EE^*$  and  $E^*E^*$  vs. time, catalyzed by  $.051M L_2(CO)ClIr$  at  $70^\circ$ .





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