at 3500 and 1650 cm^{-1} (H_2O) were unchanged after the thermal treatment.
(15) J. Selbin, *J. Chem. Educ.*, **41**, 86 (1964).
(16) S. J. Lippard and B. J. Russ, *Inorg. Chem.*, **6**, 1943 (1967).
(17) P. C. H. Mitchell and R. J. P. Williams, *J. Chem. Soc.*, 1912 (1960).
(18) B. M. Chadwick and A. G. Sharpe, *Adv. Inorg. Chem. Radiochem.*, **8**, 86 (1966).
(19) D. A. White, A. J. Solodar, and M. M. Baizer, *Inorg. Chem.*, **11**, 2160 (1972).
(20) S. F. A. Kettle and R. V. Parish, *Spectrochim. Acta*, **21**, 1087 (1965).
(21) J. Van de Poel and H. J. Newmann, *Inorg. Chem.*, **7**, 2086 (1968).
(22) A. Samotus, M. Dudek, and A. Kanas, *J. Inorg. Nucl. Chem.*, **37**, 943 (1975).
(23) A. G. Sharpe, "The Chemistry of Cyano Complexes of the Transition Metals", Academic Press, London, 1976, p 177.
(24) Although eq 3 includes O_2 as a reactant, it was shown that **4** could also be obtained in the absence of oxygen.
(25) The oxidation state Mo(V) was established by a Ce(IV) titration.[26]
(26) N. H. Furman and W. M. Murray, *J. Am. Chem. Soc.*, **58**, 1689 (1936).
(27) H. Mimoun, I. Serée de Roch, and L. Sajus, *Bull. Soc. Chim. Fr.*, 1481 (1969).
(28) J. Kaloustian, D.Sc. Thesis, Université Aix-Marseille III, 1973.
(29) Venezuelian CONICIT Fellow.
(30) On sabbatical leave from Department of Chemistry, Lowell University, Mass. 01854.

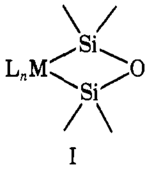
Henri Arzoumanian,* Rafael Lopez Alvarez[29]
Albert D. Kowalak,[30] **Jacques Metzger**
IPSOI, Université Aix-Marseille III
Rue H. Poincaré, St-Jérôme, 13013-Marseille, France

Received February 2, 1977

Catalysis of Siloxane Metathesis by Cyclometalladisiloxanes. Mechanistic Similarities to Olefin Metathesis Catalysis

Sir:

We wish to report that small-ring metallocycles of type I catalyze the disproportionation of 1,1,3,3-tetramethyldisiloxane (TMDS) into dimethylsilane and higher siloxane oligomers (eq 1).



I

$$(n+1)\text{TMDS} \rightarrow \underset{E'D_nE'}{Me_2SiH(OSiMe_2)_nOSiHMe_2} + nMe_2SiH_2 \qquad (1)$$

In this reaction strong Si-O bonds are broken and re-formed at room temperature in a *neutral* milieu. To our knowledge, this represents the first observation of Si-O bond rearrangements under such mild conditions.[1,2]

Eaborn et al.[3] prepared the first complex of type I, $L_2Pt(SiMe_2OSiMe_2)$, by refluxing a benzene solution of TMDS with $L_2Pt(C_2H_4)$ (L = Ph_3P). We have prepared the palladium analogue from TMDS and L_2PdCl_2. The metallocycle, $L_2Pd(SiMe_2OSiMe_2)$, mp 142 °C dec, is obtained in 20-30% yield following purification by column chromatography over Florisil (^{1}H NMR δ 7.2 (15, Ph), 0.1 (6, Me)). The iridium metallocycle, $L_2Ir(CO)(H)(SiMe_2OSiMe_2)$ (II), was prepared by stirring a benzene solution of TMDS with Vaska's compound at room temperature for ~20 min. Complex II melts at 150 °C dec and exhibits ν_{CO} and ν_{IrH} bands at 1950 and 2030 cm^{-1}, respectively. The methyl resonances of II occur as two equally intense singlets at δ 0.2 and 0.4, showing that the methyl groups are in nonequivalent environments in solution.

Wilkinson's catalyst, L_3RhCl, also reacts readily with TMDS to give a pale yellow solution, from which a bright yellow powder can be isolated. This substance is thermally labile and rapidly darkens at room temperature under a nitrogen atmosphere. The powder decomposes at 135-140 °C and its ^{1}H NMR spectrum shows a phenyl multiplet at δ 7.2 (15) and a methyl singlet at 0.2 (6). No RhH peak is observed in the IR. The exact nature of this complex is not yet established, although the IR spectrum in the SiOSi region resembles those of the platinum and palladium metallocycles.

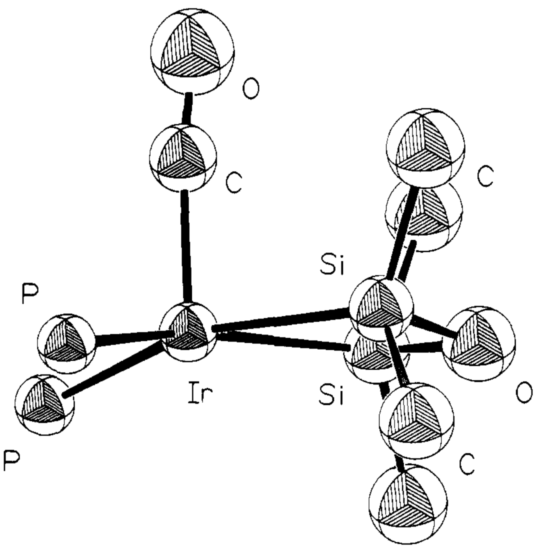


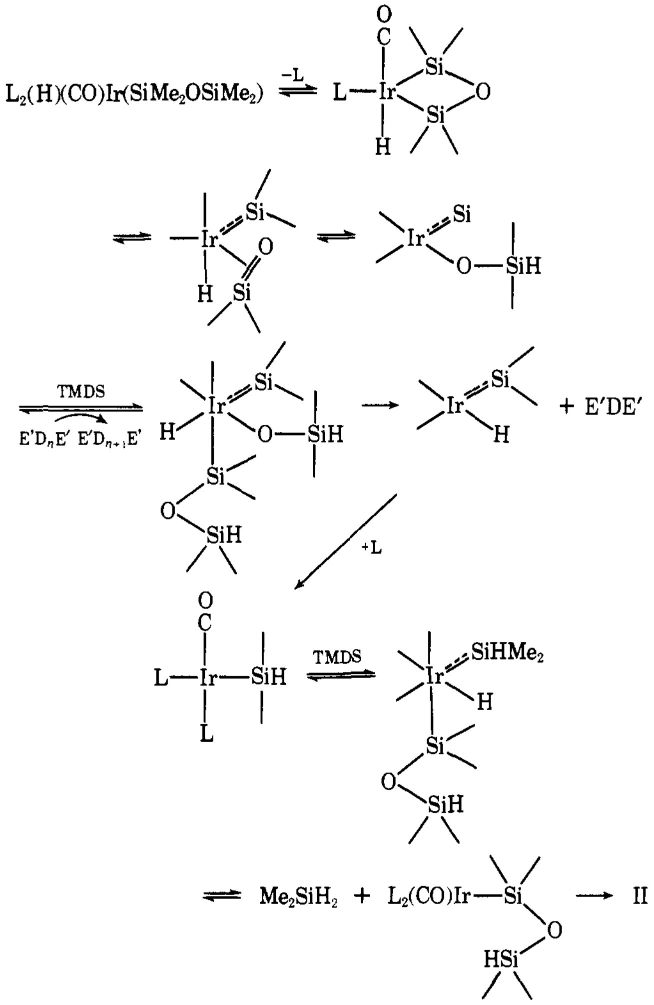
Figure 1. ORTEP drawing of the structure of hydrido-1,3-(1,1,3,3-tetramethyldisiloxanyl)carbonylbis(triphenylphosphine)iridium(III).

The molecular structure of the iridium metallocycle (II) has been determined by x-ray diffraction.[4] Figure 1 is an ORTEP drawing of the structure of the inner coordination sphere. The hydrogen presumably sits in the vacant coordination site below the basal plane. The IrSiOSi ring is folded along the Si···Si axis so that the displacements from the mean plane of the four atoms are Ir (−0.04), Si (+0.06), Si (+0.06), and O (−0.08) Å. The iridium is also displaced 0.26 Å out of the basal P_2Si_2 plane toward the carbonyl group. The Ir-Si bond distances are essentially identical at 2.40 Å and are just slightly longer than the Ir-P distance, 2.38 Å. Hence, the Ir-Si distances appear to be normal, since the covalent radii of P and Si are within 0.04 Å of each other, as judged by a variety of P-X and Si-X bond lengths.[5] The Si-O bond lengths are 1.67 and 1.70 Å and appear to be slightly longer than Si-O bonds in unstrained siloxanes (av Si-O $\simeq$ 1.63-1.65 Å).[5,6]

The angles associated with the IrSiOSi ring reflect the strain in this system. The internal angles are 99.6° (SiOSi), 97.5° (IrSiO), and 64.6° (SiIrSi). In an ideal octahedral complex, the SiIrSi angle would be 90°, so that the observed angle reflects the small bite angle of the SiOSi chelate. The SiOSi angle is also greatly compressed. In linear and higher cyclic siloxanes, the SiOSi angle falls in the 130-160° range.[5] The large SiOSi angle in siloxanes has been ascribed to the effects of (p-d) π bonding, so that a decrease of this angle may reflect some loss of (p-d) π back-donation from oxygen. This in turn would lead to a weakening (and lengthening) of the Si-O bond, as observed.

The catalytic effect of metallocycles I on excess TMDS is remarkable in that catalytic amounts of these metallocycles induce a disproportionation of TMDS into dimethylsilane and higher polysiloxanes, $E'D_nE'$ (eq 1). In addition, the rhodium complex gives cyclic, D_3 and D_4, oligomers. The platinum and palladium metallocycles are poor catalysts for eq 1. The rates are low and the catalytic effect diminishes after a few turnovers. On the other hand, the iridium and rhodium catalysts seem to be indefinitely active, the reactions are clean and rapid

Scheme I



at room temperature, and the catalyst may be recovered as long as excess TMDS is present.

To date, all the data which we have are consistent with a mechanism in which the cyclometalladisiloxane ring cleaves to form a coordinated dimethylsilylene and a coordinated Si=O double bond (Scheme I).[7,8] This step is analogous to the scission of metallacyclobutane intermediates in proposed mechanisms for the olefin metathesis reaction.[9] A sequence of oxidative-addition reactions of Si-H bonds and reductive-elimination of Si-O bonded species results in the initial formation of E'DE' and dimethylsilane as shown in Scheme I. As the concentration of E'DE' increases, this trimer may add to the iridium complex in place of TMDS, leading to the production of $E'D_2E'$ and dimethylsilane. The higher oligomers are then formed sequentially according to eq 2.

$$E'D_nE' + TMDS \rightarrow E'D_{n+1}E' + Me_2SiH_2 \qquad (2)$$

The implications of our observations are several and important. With proper control of rates, silicone polymers with perfectly alternating groups may be prepared. Stereochemically preferred configurations of the ring could lead to stereoregular silicone polymers in analogy with the Ziegler-Natta catalyzed polymerization of olefins. Finally, our observations represent the first demonstration that a well-defined, four-membered metallocycle can readily decompose under thermal conditions in the manner postulated for the olefin metathesis reaction.[10] Indeed, our results suggest that such a decomposition mode may be general to four-membered metallocycles and opens the prospect of using multiple bond chemistry for elements which do not form stable multiple bonds.

Acknowledgment. The authors are grateful to Dr. William Butler for his assistance in the x-ray work and to the Dow Corning Corp. for financial support.

References and Notes

(1) M. R. Stober, M. C. Musolf, and J. L. Speier, *J. Org. Chem.* **30**, 1651 (1965), have observed an exchange on silicon of Me_3SiO and Me groups catalyzed by H_2PtCl_6 at temperatures up to 140 °C.

(2) H. F. Stewart, *J. Organometal. Chem.*, **10**, 229 (1967), observed that reaction 1 could be effected by acidic clays at 60–100 °C.

(3) C. Eaborn, T. N. Metham, and A. Pidcock, *J. Organometal. Chem.*, **54**, C3 (1973).

(4) Crystals from CH_2Cl_2/EtOH were triclinic, $a = 12.604$, $b = 12.470$, $c = 15.821$ Å, $\alpha = 66.93$, $\beta = 105.34$, $\gamma = 112.41°$, $V = 2105$ Å^3, $Z = 2$. The space group is $P1$ (no. 2, C_i^1). The data were collected on a Syntex $P1$ diffractometer with Mo Kα radiation, giving 4580 unique reflections with $I > 3\sigma(I)$. The structure has been refined isotropically to $R = 0.078$ and $R_w = 0.106$. An absorption correction has now been applied and the refinement is continuing.

(5) A. F. Wells, "Structural Inorganic Chemistry", 3rd ed, Oxford Clarendon Press, 1962.

(6) (a) V. E. Shklover, A. E. Kalinin, A. I. Gusev, N. G. Bokii, Yu. T. Struchkov, K. A. Andrianov, and I. M. Petrova, *Zh. Strukt, Khim.*, **14**, 629 (1973); (b) V. E. Shklover, N. G. Bokii, Yu. T. Struchkov, K. A. Andrianov, B. G. Zavin, and V. S. Sulstunov, *ibid.*, **15**, 90 (1974).

(7) Dimethylsilylene complexes have been proposed as reaction intermediates, and several stable germylene and stannylene complexes are known. See (a) J. D. Cotton, P. J. Davison, D. E. Goldberg, M. F. Lappert, and K. M. Thomas, *J. Chem. Soc., Chem. Commun.*, 893 (1974); (b) P. Jutzi and W. Steiner, *Angew. Chem.*, **88**, 720 (1976); (c) P. Jutzi and W. Steiner, *Chem. Ber.*, **109**, 1575 (1976); (d) H. Okinoshima, Y. Yamamoto, and M. Kumada, *J. Am. Chem. Soc.*, **94**, 9263 (1972); (e) H. Sakurel, Y. Kamiyami, and Y. Nakadaira, *ibid.*, **97**, 931 (1975).

(8) Silicon-oxygen doubly-bonded species have been proposed as reaction intermediates. See (a) C. M. Golino, R. D. Bush, and L. H. Sommer, *J. Am. Chem. Soc.*, **97**, 7371 (1975); (b) T. J. Barton and J. A. Kilgour, *ibid.*, **98**, 7231 (1976), and references therein.

(9) (a) T. J. Katz and R. Rothchild, *J. Am. Chem. Soc.*, **98**, 2519 (1976); (b) R. H. Grubbs, D. D. Carr, C. Hoppin, and P. L. Burk, *ibid.*, **98**, 3478 (1976); (c) C. P. Casy and T. J. Burkhardt, *ibid.*, **96**, 7808 (1974); (d) P. G. Gassman and T. H. Johnson, *ibid.*, **98**, 6055 (1976).

(10) M. Ephretikhine and M. L. H. Green, *J. Chem. Soc., Chem. Commun.*, 926 (1976), have observed the photochemical decomposition of molybdenum and tungsten metallacyclobutanes to products consistent with scission of the ring to carbene-metal complex and olefin.

John Greene, M. David Curtis*
Department of Chemistry, The University of Michigan
Ann Arbor, Michigan 48109
Received April 4, 1977

Orbital Symmetry and the Benzene ⇄ Benzvalene Interconversion

Sir:

A recent review of the photochemistry of benzene[1] has prompted me to try to clear up a misunderstanding regarding the application of the orbital symmetry arguments to some of the reactions. The particular case to which I will direct myself is the benzene-benzvalene interconversion. In this reaction a bicyclobutane entity is formed from two π bonds. Therefore it is of interest to consider first what can be said about this process in itself.

On pp 31 and 34 Woodward and Hoffmann[2] state that the butadiene → bicyclobutane reaction is an example of the case where there is no symmetry element of the right type to analyze the reaction. Straightforward construction of a correlation diagram "can only lead to the conclusion—often false—that a reaction is symmetry allowed". On pp 75-78 they consider the reaction again. The bicyclobutanes are formed from butadienes by irradiation and are found to be remarkably stable. The activation energy for isomerization to butadiene is 41 kcal/mol. This thermal process is interpreted as an allowed $[{}_\sigma 2_s + {}_\sigma 2_a]$ reaction and the observed stereochemistry tallies. Apparently this conversion for which the correlation diagram would have shown allowed character in all modes will in fact