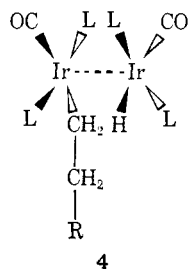


terms of the coordinative unsaturation of  $\text{HIr}(\text{CO})\text{L}_2$ . This species, postulated to be generated *in situ*, would be expected to rapidly coordinate a fifth ligand (*e.g.*, L), and the bimolecular reaction discussed can be envisioned as one in which, initially, a metal-metal bond forms by coordination of nucleophilic species 1 to the unsaturated hydride. Such an interaction leads to short-lived intermediate 4, a species whose structure is



reminiscent of  $d^8$  stacked Ir(I) complexes which have been observed crystallographically.<sup>20</sup> Loss of octane from this aggregate might be accomplished through intermediacy of bridging hydride and/or alkyl ligands.<sup>21</sup>

**Acknowledgment.** The authors gratefully acknowledge support for this work given by the donors of the Petroleum Research Fund, administered by the American Chemical Society, and by the Research Corporation. They also thank Professor Jack R. Norton and Dr. Jay A. Labinger for helpful comments and suggestions.

(20) L. V. Interrante and F. P. Bundy, *Chem. Commun.*, 584 (1970).

(21) Such a process has recently been suggested: P. S. Braterman and R. J. Cross, *Chem. Soc. Rev.*, 2, 271 (1973).

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### Evidence for the Generation of Silicon-Silicon, Silicon-Oxygen, and Silicon-Carbon Double Bonds in a Single Reaction

Sir:

Evidence consistent with the transient existence of molecules containing (p-p) $\pi$  bonded silicon<sup>1-3</sup> and germanium<sup>4,2d</sup> has accumulated in the last few years to a degree that little doubt remains, although the nature of bonding (*e.g.*, diradical character) remains in question. We wish to report a novel reaction which can

(1)  $\text{Si}=\text{Si}$ : D. N. Roark and G. J. D. Peddle, *J. Amer. Chem. Soc.*, 94, 5837 (1972).

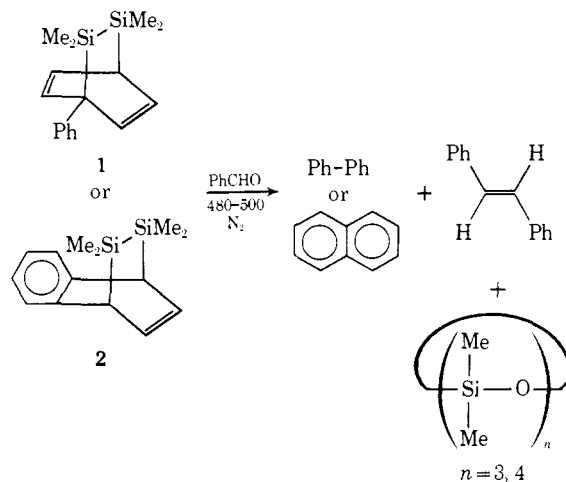
(2)  $\text{Si}=\text{O}$ : (a) L. E. Gusel'nikov, *et al.*, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 6, 84 (1971); (b) I. M. T. Davidson and J. F. Thompson, *Chem. Commun.*, 251 (1971); (c) T. J. Barton, C. L. McIntosh, and E. A. Kline, 3rd International Symposium on Organosilicon Chemistry, Madison, Wis., Aug 1972; (d) T. J. Barton, E. A. Kline, and P. M. Garvey, *J. Amer. Chem. Soc.*, 95, 3078 (1973); (e) P. Boudjouk and L. H. Sommer, *J. Chem. Soc., Chem. Commun.*, 54 (1973); (f) D. N. Roark and L. H. Sommer, *ibid.*, 167 (1973).

(3)  $\text{Si}=\text{C}$ : (a) N. S. Nametkin, V. M. Vdovin, L. E. Gusel'nikov, and V. I. Zavyalov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 3, 534 (1966); (b) M. C. Flowers and L. E. Gusel'nikov, *J. Chem. Soc. B*, 419 (1968); (c) R. P. Clifford, B. G. Gowenlock, C. A. F. Johnson, and J. Stevenson, *J. Organometal. Chem.*, 34, 53 (1972); (d) I. M. T. Davidson and C. A. Lambert, *J. Chem. Soc. A*, 882 (1971); (e) T. J. Barton and C. L. McIntosh, *J. Chem. Soc., Chem. Commun.*, 861 (1972); (f) T. J. Barton and E. A. Kline, *J. Organometal. Chem.*, 42, C21 (1972); (g) P. Boudjouk, J. R. Roberts, C. M. Golino, and L. H. Sommer, *J. Amer. Chem. Soc.*, 94, 7926 (1972); (h) ref 2e; (i) ref 2f.

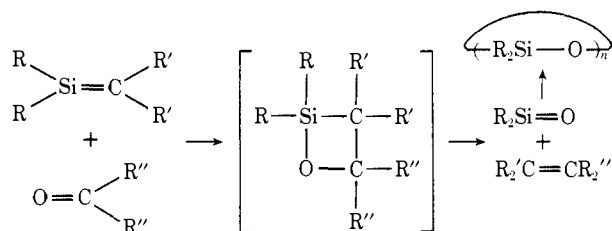
(4) M. D. Curtis, *J. Amer. Chem. Soc.*, 91, 6011 (1969).

best be explained by invoking the intermediacy of compounds containing the silicon-silicon, silicon-oxygen, and silicon-carbon double bonds, respectively.

Roark and Peddle<sup>1</sup> have reported strong evidence that 7,8-disilabicyclo[2.2.2]octa-2,5-dienes thermally aromatize through extrusion of a disilene ( $\text{R}_2\text{Si}=\text{SiR}_2$ ). We find that copyrolysis of either 1-phenyl-7,7,8,8-tetramethyl-7,8-disilabicyclo[2.2.2]octa-2,5-diene<sup>1</sup> (1) or 5,6-benzo-7,7,8,8-tetramethyl-7,8-disilabicyclo[2.2.2]octa-2,5-diene (2) and an excess (20:1) of benzaldehyde in a flow system ( $\text{N}_2$ , 480-500°) affords the expected biphenyl or naphthalene together with *trans*-stilbene (23.9%)<sup>5</sup> and a mixture of hexamethylcyclotrisiloxane and octamethylcyclotetrasiloxane (16 and 13.8%, respectively).<sup>5</sup>



The recent demonstration<sup>2e-f</sup> that silaalkenes ( $\text{R}_2\text{Si}=\text{CR}_2'$ ) undergo cycloaddition to the carbonyl group to produce an unstable silaoxetane which thermally decomposes to an olefin and a silanone ( $\text{R}_2\text{Si}=\text{O}$ ) which undergoes cyclic oligomerization is crucial in understanding the reaction of 1 or 2 with benzaldehyde.

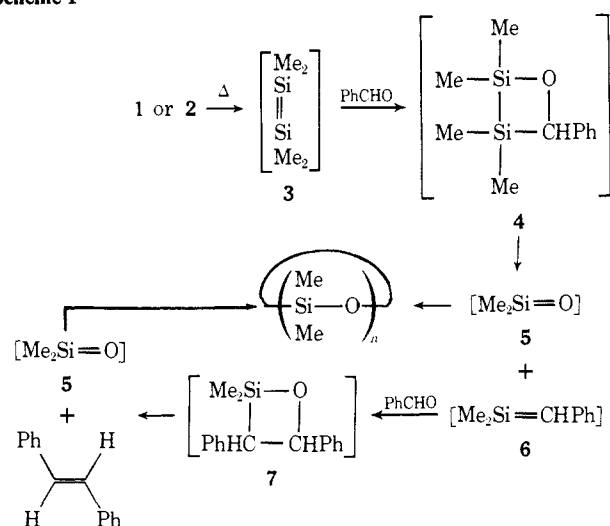


In view of this sequence we propose a mechanism (Scheme I) where initially formed tetramethyldisilene (3) adds to benzaldehyde to form an intermediate disilaoxetane (4). Thermal cleavage of 4 generates both a silanone (5) and a silaalkene, 1-phenyl-2-methyl-2-silapropene (6). Oligomerization of 5 leads to the observed mixture of cyclosiloxanes while 6 can react further with benzaldehyde to form silaoxetane, 7. Finally, extrusion of a second molecule of 5 from 7 affords *trans*-stilbene.

It is difficult to exclude the possibility that *trans*-stilbene arises from dimerization of phenylcarbene (8). Indeed a reasonable route can be written by assuming stepwise attack by 3 on carbonyl followed by extrusion of 8. The cyclosiloxanes could again be formed

(5) Positive identification of products was made by spectral comparison with authentic samples. Yields are taken from calibrated gc traces.

Scheme I



through silanone (5) intermediacy. However, the absence of the normal gas-phase isomerization products of 8 from our reaction mixtures is sufficient for tentative exclusion of such a mechanism.<sup>6-8</sup>

The dramatic reaction reported here emphasizes the necessity of invoking (p-p) $\pi$  bonded silicon in a variety of reactions. We are continuing our efforts to prepare a stable molecule containing a (p-p) $\pi$  bonded silicon so that the exact nature of the bonding can be determined.

**Acknowledgment** is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, and to the Research Corporation for support of this research.

(6) Pyrolysis of the sodium salt of benzaldehyde tosylhydrazone (250°, 40 Torr, N<sub>2</sub> flow) is reported to afford 15% stilbenes and 30% heptafulvalene.<sup>7</sup> It has been concluded that, in the gas phase, phenylcarbene (8) undergoes ring expansion to cycloheptatrienyldiene at temperatures  $\leq 600^\circ$  and ring contraction to fulvenallene above 600°.<sup>8</sup> Our product mixture (trapped at  $-196^\circ$ ) was only slightly yellow, both before and after warming under nitrogen, thus indicating an absence of heptafulvalene which was confirmed by nmr. Pyrolysis of 2, PhCHO and cyclohexene (1:4:10) did not afford any detectable 7-phenylnorcaradiene.

(7) R. C. Joines, A. B. Turner, and W. M. Jones, *J. Amer. Chem. Soc.*, **91**, 7754 (1969).

(8) P. Schissel, M. E. Kent, D. J. McAduo, and E. Hedaya, *J. Amer. Chem. Soc.*, **92**, 2147 (1970).

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### Temperature and Axial Ligand Dependence of the Dynamic Character of Allylcobaloximes

Sir:

Organocobaloximes have been widely studied because of the many similarities between their chemistry and that of vitamin B<sub>12</sub> coenzyme and analogous cobalamins.<sup>1</sup> Though there is excellent evidence for the formation of transient olefinic  $\pi$ -complexes in solution,<sup>2</sup>

(1) (a) D. Dodd and M. D. Johnson, *J. Organometal. Chem.*, **52**, 1 (1973); (b) J. M. Pratt, "The Inorganic Chemistry of Vitamin B<sub>12</sub>," Academic Press, New York, N. Y., 1972.

(2) (a) B. T. Golding, H. L. Holland, U. Horn, and S. Sakrikar, *Angew. Chem., Int. Ed. Engl.*, **9**, 959 (1970); (b) B. T. Golding and S. Sakrikar, *J. Chem. Soc., Chem. Commun.*, 1183 (1972); (c) E. A. Parfenov, T. G. Chervyakova, and A. M. Yurkevich, *Zh. Obshch. Khim.*, **42**, 2584 (1972); (d) R. B. Silverman, D. Dolphin, and B. M. Babior, *J.*

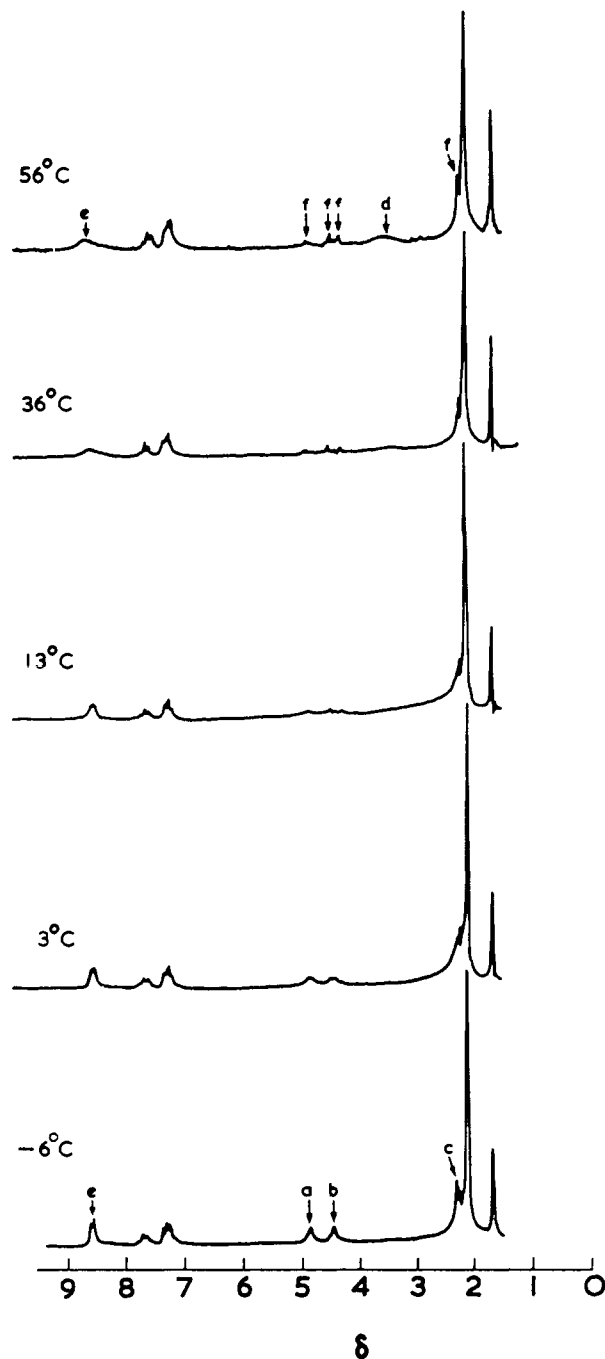


Figure 1. Temperature dependence of the 100-MHz <sup>1</sup>H nmr spectrum of I (CDCl<sub>3</sub>). Impurities<sup>7</sup> (marked f) are evident in the region of δ 4-5 above 10°.

only  $\sigma$ -bonded organocobaloximes and -cobalamins have been isolated,<sup>3</sup> and it has been generally assumed that the similar character of the carbon-cobalt bonds in these complexes is largely a result of the steric and electronic effect of the relatively inflexible equatorial ligand and, to a lesser extent, of the other axial ligand.

We now report that the character of allylcobaloximes is dependent upon the nature of the other axial ligand and that, in some cases, dynamic  $\sigma$ -allylcobaloximes are formed. Thus, at  $-6^\circ$  and below, the 100-MHz <sup>1</sup>H nmr spectrum (CDCl<sub>3</sub>; Figure 1) of 2-methylallylbis-

*Amer. Chem. Soc.*, **94**, 4028 (1972); (e) R. B. Silverman and D. Dolphin, *ibid.*, **95**, 1686 (1973).

(3) Reference 1a Table I, gives a comprehensive list of such compounds.