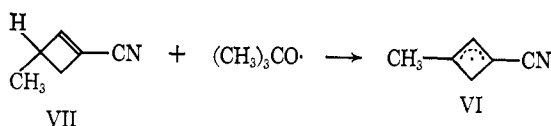


2.73 G (1:1:1 triplet). Interestingly, the radical species VI is also obtained when 3-methylcyclobutene-1-carbonitrile (VII) is subjected to *t*-butoxy radicals, indicating that the tertiary allylic hydrogen in VII is much



more reactive toward homolytic abstraction than the two secondary allylic hydrogens.

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Hydrogen-Bridged Silicon-Rhenium Bonds. A Diphenylsilane Complex of Rhenium Carbonyl

Sir:

The role of hydrogen as a bridging group between two transition metals is now well established as, for example, in the molecules $\text{C}_6\text{H}_5(\text{CO})_2\text{Mo}(\text{H})(\text{P}(\text{CH}_3)_2)_2\text{Mo}(\text{CO})_2\text{C}_6\text{H}_5$ ¹ and $(\text{OC})_4\text{Mn}(\text{H})(\text{P}(\text{C}_6\text{H}_5)_2)_2\text{Mn}(\text{CO})_2$ ² and in various polynuclear carbonyl hydrides of manganese and rhenium.³ Hydrogen bridges between a main group element and a transition metal have heretofore been encountered only for boron, as in the compounds $\text{HMn}_3(\text{CO})_{10}(\text{BH}_3)_2$,⁴ $[(\text{CH}_3)_4\text{N}][\text{Cr}(\text{CO})_4\text{B}_3\text{H}_8]$,⁵ and $[(\text{C}_6\text{H}_5)_3\text{P}]_2\text{CuBH}_4$.⁶ We now report such a mixed hydrogen bridge involving silicon as the main group element.

The first compound of this new class is $(\text{C}_6\text{H}_5)_2\text{SiH}_2\text{Re}_2(\text{CO})_8$, prepared by ultraviolet irradiation of a benzene solution of $\text{Re}_2(\text{CO})_{10}$ and $(\text{C}_6\text{H}_5)_2\text{SiH}_2$ at room temperature under a nitrogen atmosphere. After removal of solvent and unreacted starting materials under vacuum, the residual solid was crystallized three times from *n*-hexane to afford colorless, moderately air-stable crystals of the product,⁷ mp 168–169°. The mass spectrum established that 12 hydrogen atoms were present in the molecule. The nmr spectrum (taken on a CCl_4 solution, in which, rather surprisingly, the com-

pound is stable for long periods) exhibited a peak at τ 19.56 of about one-fifth the intensity of the phenyl protons. Further investigation by infrared and nmr (*vide infra*) suggested that a transition metal hydride of novel type was involved, and a single-crystal X-ray diffraction study was undertaken to establish the structure more rigorously.

The complex was found to crystallize in the orthorhombic space group Pbcn with eight molecules per unit cell. Three-dimensional intensity data were collected on a PAILRED automated diffractometer, and the structure was solved by conventional methods. At the present state of refinement the *R* factor is 5.7% for 1300 unique above-background reflections. All non-hydrogen atoms have been located and anisotropic temperature factors assigned to the rhenium and silicon atoms. The molecular structure is shown in Figure 1, in which the unique pair of hydrogen atoms has been placed in the conspicuously vacant sixth coordination site of each rhenium. This inference is strongly supported by spectroscopic evidence mentioned later. If the hydrogen atoms are placed in the Re–Si–Re plane, with a Re–H distance of 1.68 Å⁸ at right angles to the Re–Re bond, the Si–H distance is 1.57 Å, not unreasonable in comparison with the value of 1.48 Å found in SiH_4 ,⁹ and certainly consistent with a bridging rather than a terminal hydrogen. It is of interest that the molecular symmetry is 2 mm (C_{2v}), although none is required crystallographically; there are no significant deviations from it.

The infrared spectrum of $(\text{C}_6\text{H}_5)_2\text{SiH}_2\text{Re}_2(\text{CO})_8$ showed carbonyl stretching bands (with relative intensities) at 2110 (3.2), 2075 (6.7), 2021 (7.7), 2015 (10), 2000 (7.2), 1995 (4.5), and 1977 (7.9) cm^{-1} (cyclohexane). The over-all band pattern resembled that of $(\text{C}_6\text{H}_5)_2\text{GeFe}_2(\text{CO})_8$,¹⁰ suggesting a similar geometry for the heavy-atom framework in both molecules. The possibility that one or more bands in the carbonyl region was due to $\nu(\text{Re–H})$ was excluded by examining the infrared spectrum of $(\text{C}_6\text{H}_5)_2\text{SiD}_2\text{Re}_2(\text{CO})_8$.¹¹ The spectra of the two compounds were almost identical except for minor changes ($\leq 3 \text{ cm}^{-1}$) in some of the carbonyl stretching bands; this effect is due to altered mixing of $\nu(\text{CO})$ with an unobserved H or D mode.¹² In particular, the 1600–1200- cm^{-1} region, where terminal $\nu(\text{Re–D})$ would be expected, was unchanged.

The mass spectrum of $(\text{C}_6\text{H}_5)_2\text{SiH}_2\text{Re}_2(\text{CO})_8$ provides further evidence for bridging hydrogens. As noted above, the molecular ion of the compound was observed, and a comparison of ion intensities with the theoretical multiplet pattern¹³ established that there is no appreciable hydrogen loss from the molecular ion.¹⁴

(1) R. J. Doedens and L. F. Dahl, *J. Am. Chem. Soc.*, **87**, 2576 (1965); R. G. Hayter, *Inorg. Chem.*, **2**, 1031 (1963).

(2) R. J. Doedens, W. T. Robinson, and J. A. Ibers, *J. Am. Chem. Soc.*, **89**, 4323 (1967); R. G. Hayter, *ibid.*, **86**, 823 (1964).

(3) M. R. Churchill, P. H. Bird, H. D. Kaesz, R. Bau, and B. Fontal, *ibid.*, **90**, 7135 (1968); H. D. Kaesz, R. Bau, and M. R. Churchill, *ibid.*, **89**, 2775 (1967); J. M. Smith, K. Mehner, and H. D. Kaesz, *ibid.*, **89**, 1759 (1967); H. D. Kaesz, V. Fontal, R. Bau, S. W. Kirtley, and M. R. Churchill, *ibid.*, **91**, 1021 (1969); A. P. Ginsberg and M. K. Hawkes, *ibid.*, **90**, 5930 (1968).

(4) H. D. Kaesz, W. Fellman, G. R. Wilkes, and L. F. Dahl, *ibid.*, **87**, 2753 (1965).

(5) F. Klanberg, E. L. Muetterties, and L. J. Guggenberger, *Inorg. Chem.*, **7**, 2272 (1968).

(6) S. J. Lippard and K. M. Melmed, *ibid.*, **6**, 2223 (1967).

(7) Anal. Calcd for $\text{C}_{20}\text{H}_{12}\text{O}_8\text{Re}_2\text{Si}$: C, 30.77; H, 1.55; Si, 3.60. Found: C, 30.67; H, 1.77; Si, 3.68.

(8) S. C. Abrahams, A. P. Ginsberg, and K. Knox, *Inorg. Chem.*, **3**, 558 (1964).

(9) A. F. Wells, "Structural Inorganic Chemistry," 3rd ed, Oxford University Press, London, England, 1962, p 696.

(10) E. H. Brooks, M. Elder, W. A. G. Graham, and D. Hall, *J. Am. Chem. Soc.*, **90**, 3587 (1968).

(11) This compound was prepared by the same method using $(\text{C}_6\text{H}_5)_2\text{SiD}_2$. Carbonyl stretching bands (with relative intensities) are observed at 2110 (3.0), 2076 (6.4), 2018 (8.8) sh, 2016 (10), 1998 (7.9), 1995 (5.2), and 1975 (7.4) cm^{-1} in cyclohexane solution.

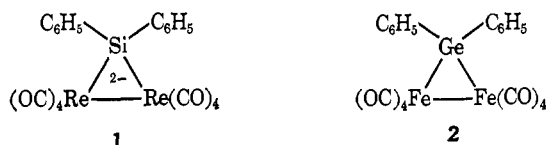
(12) Shifts in $\nu(\text{CO})$ upon deuteration have previously been observed; cf. the analysis by P. S. Braterman, R. W. Harrill, and H. D. Kaesz, *J. Am. Chem. Soc.*, **89**, 2851 (1967), and references cited.

(13) The computed multiplet pattern is (nominal mass, relative abundance): 778 (28.8); 779 (8.1); 780 (100); 781 (27.6); 782 (91.0); 783 (24.2); 784 (7.0); 785 (0.8); 786 (0.1). Peaks at 776 or 777 would indicate hydrogen loss.

The series $[(C_6H_5)_2SiH_2Re_2(CO)_n]^+$ is the most intense in the spectrum, although all ions below the parent (*i.e.*, $0 \leq n \leq 7$) show considerable hydrogen loss. It appears that hydrogen in this compound is lost with somewhat greater ease than in $HMn_3(CO)_{10}(BH_3)_2$, in which hydrogen loss commences only after the loss of three carbonyl groups.¹⁵

The most convincing evidence for placing the hydrogen atoms as in Figure 1 is provided by the nmr spectrum of the dimethylsilicon analog, $(CH_3)_2SiH_2Re_2(CO)_8$.¹⁶ The CH_3 proton resonance appeared as a 1:2:1 triplet centered at τ 8.87, with $J = 1.5$ Hz (CCl_4 solution). The resonance at τ 20.56 was broad, consistent with an unresolved septuplet, and upon irradiation at the high-field frequency the triplet collapsed to a singlet. The high-field protons are thus magnetically equivalent, and most probably in symmetrically equivalent positions in the $SiRe_2$ plane.¹⁷ The magnitude of the coupling may also be compared with the value of 4.2 Hz in $(CH_3)_2SiH_2$ itself, and suggests that the high-field protons are proximate to the dimethylsilicon moiety.

Structurally, the molecule bears some relation to rhenium carbonyl, but has an eclipsed conformation and a slightly longer rhenium-rhenium bond length (3.121 *vs.* 3.02 Å¹⁸). From this viewpoint, each silicon-hydrogen bond functions as a two-electron donor to rhenium, effectively taking the place of a carbonyl group; the interaction could be described as a three-center, two-electron bond with the two electrons supplied by the original Si-H bond. Alternatively the molecule could be described as a protonated form of the (as yet hypothetical) anion **1**, which is isoelectronic with the known stable compound **2**.¹⁰



These compounds were prepared in the course of a program on photochemical reactions of metal carbonyls with silanes, some results of which have very recently been reported.¹⁹ Hydrides other than silanes are also under investigation. It appears that in addition to their inherent interest, molecules such as those reported here will be useful in the synthesis of other compounds. Thus, $(C_6H_5)_2SiH_2Re_2(CO)_8$ is readily converted to the new dimeric hydride $[HRe(CO)_4]_2$; infrared spectra suggest that the latter has a hydrogen-bridged structure of D_{2h} symmetry. Further details will be reported when the crystal structure has been completed.²⁰

(14) This would not be expected for a terminally bonded hydrogen, such as $HMn(CO)_5$, where hydrogen loss is competitive with CO loss for all species: W. F. Edgell and W. M. Risen, Jr., *J. Am. Chem. Soc.*, **88**, 5451 (1966).

(15) J. M. Smith, K. Mehner, and H. D. Kaesz, *ibid.*, **89**, 1759 (1967).

(16) This compound was prepared in a closed vessel with intermittent release of carbon monoxide. The pale yellow, moderately air-stable crystals melt with decomposition at 115° and show infrared carbonyl bands at 2109, 2072, 2021, 2010, 1998, and 1978 cm^{-1} (cyclohexane). Satisfactory mass spectrum and microanalysis have been obtained.

(17) This argument supposes that the magnetic equivalence is neither accidental nor the result of a rapid exchange process.

(18) L. F. Dahl, E. Ishishi, and R. E. Rundle, *J. Chem. Phys.*, **26**, 1750 (1957).

(19) W. Jetz and W. A. G. Graham, *J. Am. Chem. Soc.*, **91**, 3375 (1969).

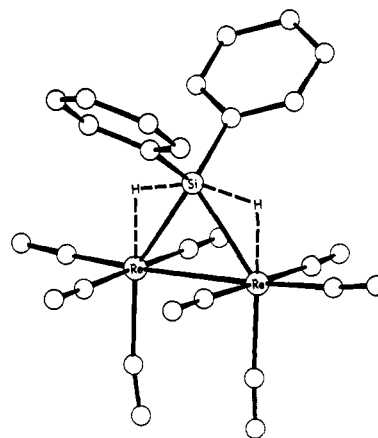


Figure 1. The molecular structure of $(C_6H_5)_2SiH_2Re_2(CO)_8$. Hydrogen atoms were not observed but are shown in the positions suggested by spectroscopic evidence (see text). Bond lengths and angles (with standard deviations) are Re-Re = 3.121 (3) Å; Re-Si = 2.51 (1) Å and 2.53 (1) Å; Re-Si-Re = 76.1 (3)°. There are no significant deviations from C_{2v} symmetry.

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(20) Research in progress by Dr. M. J. Bennett and Miss Wendy Brooks.

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Deuteron Magnetic Relaxation Times and Molecular and Intramolecular Motion in Some Organic Liquids

Sir:

There have been several recent papers describing the application of deuteron magnetic relaxation in suitably labeled molecules to the problem of the nature of molecular and intramolecular motion in liquids.¹⁻⁴ Up to date these have (a) involved molecules where intramolecular motion is expected; (b) involved the use of extrapolated values of the quadrupole coupling constants, e^2qQ/\hbar ; or (c) involved the use of values for the microviscosity factor,⁵ f , based on other than magnetic resonance measurements in the equations

$$1/T_1 = \frac{3}{8} \left(\frac{e^2qQ}{\hbar} \right)^2 \tau_c \quad (1)$$

$$\tau_c = 0.74 f \frac{\eta M}{\rho NKT} \quad (2)$$

by which one attempts to relate the observed relaxation rates, $1/T_1$, to calculated molecular reorientation times,

- (1) T. T. Bopp, *J. Chem. Phys.*, **47**, 3621 (1967).
- (2) D. E. Woessner, B. S. Snowden, Jr., and E. T. Strom, *Mol. Phys.*, **14**, 265 (1968).
- (3) M. D. Zeidler, *Ber. Bunsenges. Phys. Chem.*, **69**, 659 (1965).
- (4) D. E. Woessner, B. S. Snowden, Jr., R. A. McKay, and E. T. Strom, *J. Mag. Res.*, **1**, 89 (1969).
- (5) A. Gierer and K. Wirtz, *Z. Naturforsch.*, **8a**, 532 (1953).