Table I. ^{29}Si Chemical Shielding Parameters in Organosilicon Compounds[a]

Compound	σ_{11}	σ_{22}	σ_{33}	$\bar{\sigma}$	σ_i
$(CH_3)_4Si$	0	0	0	0	0
$(CH_3)_3SiOCH_3$	−33	−31	8	−19	−17
$(CH_3)_2Si(OCH_3)_2$	−12	−12	35	4	2.5
$CH_3Si(OCH_3)_3$	23	35	68	42	41.5
$Si(OCH_3)_4$	80	80	80	80	79.5
$[(CH_3)_3Si]_3CH$	−8	4	18	5	
$(CH_3)_3SiC_6H_5$	−2	4	29	10	4.5
$[(CH_3)_3Si]_2O$	−16	−8	14	−3	−4
$[(CH_3)_2SiO]_3$	−8	0	62	18	10[b]
$[(CH_3)_2SiO]_4$	4	4	53	20	20

[a] All values are in parts per million (±3) relative to solid TMS. $\bar{\sigma} = {}^1/_3(\sigma_{11} + \sigma_{22} + \sigma_{33})$. σ_i is the isotropic shift in the neat liquid, referred to liquid TMS (ref 3). [b] Solution in C_6H_6.

field H_0 was 22,800 G, the proton decoupling field H_1 (H) was ~8 G, and the cross-polarization field H_1 (Si) was ~40 G. Each spectrum was obtained in ~10 min of running time using ~200 mg of sample material. All values are referred to an external reference of (solid) TMS. The following points can be made about these values.

(a) The range of ^{29}Si anisotropies, like the range of isotropic ^{29}Si shifts in liquids,[3] is smaller than the corresponding range of ^{13}C values.[4]

(b) With a few exceptions (believed real) the mean shift does not change appreciably on melting. Similar behavior, including exceptions, has been observed previously for ^{13}C.[3]

(c) Deviations from axial symmetry of the shielding tensor arising from crystalline environment are sometimes seen [*cf.* $CH_3Si(OCH_3)_3$] in cases where the shielding tensor for the isolated molecule would be expected to be axial.

(d) Since these measurements are made in powders, the orientations of the principal axes in the molecular frame are not known and presumably change from compound to compound. Single-crystal studies would remove this ambiguity.

Acknowledgment. This work was supported in part by the National Institutes of Health.

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Synthesis and X-Ray Structure of Di-μ-hydrido-octacarbonyldirhenium

Sir:

The first reported polynuclear carbonyl hydride of rhenium was $H_3Re_3(CO)_{12}$,[1] *i.e.*, $[HRe(CO)_4]_3$, in which the hydrogens are considered to bridge the edges of a triangular arrangement of rhenium atoms. We now describe a new *dimeric* complex $H_2Re_2(CO)_8$, *i.e.*, $[HRe(CO)_4]_2$, which formally bears the same relation to the trimer as ethylene does to cyclopropane. It is, moreover, the analog of the well-known tetracarbonyl halide dimers of rhenium,[2] although the bonding in the hydride is less readily described in simple terms.

A sample of $Ph_2SiH_2Re_2(CO)_8$[3] (1.0 g) was stirred in chloroform (50 ml) with silicic acid (5 g) for 1 hr. The mixture was filtered and the filtrate evaporated to leave a yellow solid which afforded yellow crystals of $H_2Re_2(CO)_8$[4] (0.60 g, 78%) upon recrystallization from dichloromethane–*n*-hexane at −20°. The compound is moderately air stable, darkens above 115°, and decomposes slowly in light. The infrared spectrum exhibits bands assigned to carbonyl stretching modes (see below) at 2093 (3.5), 2020 (10.0), 2000 (8.6), and 1979 (9.8) cm^{-1} (cyclohexane, relative intensities in parentheses). A single sharp proton resonance was observed at τ 19.04 ($CDCl_3$) and shown to be due to two hydrogens using a known molar ratio of $Ph_2SiH_2Re_2(CO)_8$ as standard. An intense peak due to the molecular ion occurred in the mass spectrum, while peaks due to $[HRe_2(CO)_8]^+$ or $[Re_2(CO)_8]^+$ were not observed;[5] this characteristic is indicative of bridging positions for the hydrogens.[6]

No infrared bands that could be attributed to terminal Re–H or Re–D vibrations were observed in cyclohexane solution for $H_2Re_2(CO)_8$ in the 2200–1800-cm^{-1} region, nor for $D_2Re_2(CO)_8$ in the 1600–1200-cm^{-1} region. However, the Raman spectrum of the hydride showed bands at 1382 and 1272 cm^{-1}, shifting to 974 and 924 cm^{-1} in the deuteride, and this may be taken as an unequivocal demonstration of bridging positions for hydrogen.[7]

The compound crystallizes as prisms in the monoclinic crystal system with space group $P2_1/c$; lattice parameters a = 8.96 (2) Å, b = 11.62 (2) Å, c = 12.85 (2) Å, and β = 109.2 (1)°; four molecules per unit cell; ρ_{obsd} = 3.16 g/ml (by flotation) and ρ_{calcd} = 3.18 g/ml. The crystals decompose in the X-ray beam. This feature, coupled with the relatively large absorption effects (typically transmission factors ranged from 0.1 to 0.2 for the crystals used), severely limited the accuracy of the study. Intensity data were collected from two crystals (dimensions 0.14 × 0.11 × 0.14 mm and 0.12 × 0.13 × 0.10 mm) on a PAILRED diffractometer ($h0l$ to $h12l$) using molybdenum Kα X-radiation that

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(1) D. K. Huggins, W. Fellmann, J. M. Smith, and H. D. Kaesz, *J. Amer. Chem. Soc.*, **86**, 4841 (1964).

(2) E. W. Abel, G. B. Hargreaves, and G. Wilkinson, *J. Chem. Soc.*, 3149 (1958); M. A. El-Sayed and H. D. Kaesz, *Inorg. Chem.*, **2**, 158 (1963).

(3) J. K. Hoyano, M. Elder, and W. A. G. Graham, *J. Amer. Chem. Soc.*, **91**, 4568 (1969).

(4) *Anal.* Calcd for $C_8H_2O_8Re_2$: C, 16.06; H, 0.34; O, 21.39. Found: C, 16.17; H, 0.45; O, 21.50.

(5) The computed multiplet pattern for $[H_2Re_2(CO)_8]^+$ is (nominal mass, relative abundance) 596 (29.3), 597 (2.7), 598 (100.0), 599 (9.3), 600 (86.4), 601 (8.0), 602 (1.4). The observed pattern was in excellent agreement, with no peaks at 594 or 595 which would have indicated hydrogen loss. Further confirmation of the identity of the compound was provided by an exact mass measurement on the nominal 600 peak. Calculated intensity-weighted mean m/e for all isotope combinations contributing to the nominal 600 peak of $H_2Re_2(CO)_8$: 599.8869. Found: 599.8860.

(6) J. M. Smith, K. Mehner, and H. D. Kaesz, *J. Amer. Chem. Soc.*, **89**, 1759 (1967); B. F. G. Johnson, J. Lewis, and P. W. Robinson, *J. Chem. Soc. A*, 1684 (1970).

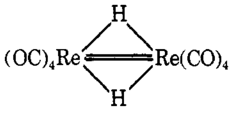
(7) We are grateful to Professor H. D. Kaesz for recording the Raman spectra of these compounds. A detailed study of the Raman modes of these and other hydrogen-bridged systems is in progress in Professor Kaesz's laboratory. *Cf.* H. D. Kaesz and S. W. Kirtley, Abstracts, 163rd National Meeting of the American Chemical Society, Boston, Mass., April, 1972, No. INOR 131.

had been monochromated using an oriented graphite crystal.

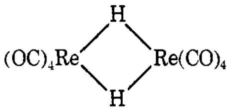
The structure has been solved from conventional Patterson and electron density maps using 1163 significant reflections ($I/\sigma(I) \geq 3.0$) collected in the range $0 < 2\theta < 41.5°$. Refinement of the structure by least squares was limited to the isotropic model in view of the obvious defects in the intensity data. This refinement has reduced the conventional R factor to 0.10. While the precision of the structure is low, the structural information on the $Re_2(CO)_8$ fragment is adequate for our purposes.

A view of the heavier atom skeleton is shown in Figure 1. Within experimental error, the structure had D_{2h} symmetry although this is not required crystallographically. The rhenium–rhenium distance of 2.90 Å is the shortest observed in a rhenium carbonyl cluster and may be compared with the hydrogen-bridged rhenium–rhenium distances of 3.17 Å in $[H_2Re_3(CO)_{12}^-]$,[8] 3.16 Å in $[H_6Re_4(CO)_{12}^{2-}]$,[9] and 3.295 (2) Å in $HRe_3(CO)_{14}$.[10] The two $Re(CO)_4$ fragments exhibit no significant angular deviations from those expected assuming that their structure is based on an octahedron (*i.e.*, all C–Re–C angles are either 90 or 180°) and all rhenium–carbon bond lengths are normal. The two hydrogen atoms would appear to be best placed in the plane defined by the rhenium atoms and the carbonyl groups labeled 2, 3, 6, and 7. This assumption is based on a consideration of intramolecular contacts and analogy to structures of the type $Mn_2(CO)_8Br_2$.[11] In view of their limited accuracy, one cannot infer from the structural results whether the hydrogen bridges are symmetrical or unsymmetrical. We assume the symmetrical structure for simplicity in the following discussion.

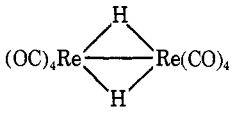
The effective atomic number rule at its simplest level would suggest that $H_2Re_2(CO)_8$ be formulated as **1**, with each hydrogen donating 0.5 electron to each rhenium and a double bond between the rhenium atoms. This highly formal description has the virtue of following precisely the electron bookkeeping system which requires no metal–metal bond in $[ClRe(CO)_4]_2$ and a single bond in $[Ph_2SiRe(CO)_4]_2$.[12]



1



2



3

Alternatively, the H_2Re_2 bridge system (like that in B_2H_6[13]) could be considered, in an equivalent orbital context, to comprise a pair of three-center, two-electron bonds as in **2**, and this formulation too is consistent with the effective atomic number rule.[14] However, in this particular case, in view of the extremely short metal–metal distance, some degree of direct metal–metal interaction seems likely; in this regard, we offer structure **3**, by which we imply the sum of a two-electron, four-center H_2Re_2 bridge and a two-electron, two-center Re–Re bond. This approach, as well as the previous ones, can be considered to satisfy the effective atomic number rule, which is clearly of limited value in formulating the compound. A complete molecular orbital treatment of this bridged dimer would be most informative and probably essential in assessing the merits of representations such as **1**, **2**, and **3**.[15]

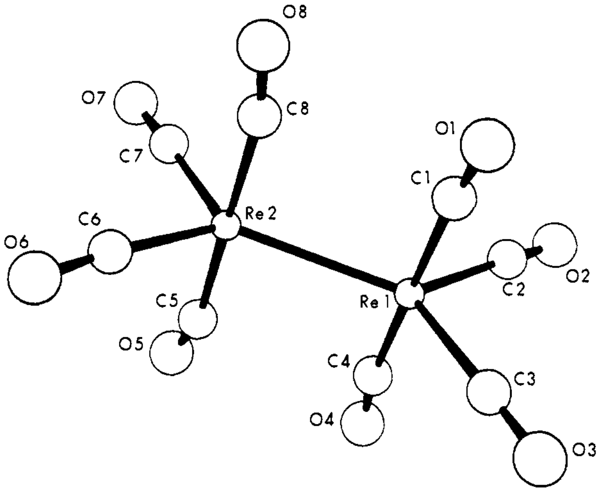


Figure 1. The molecular structure of $H_2Re_2(CO)_8$. Hydrogen atoms were not located and are not shown but are assumed to lie in the plane of carbonyl groups 2, 3, 6, and 7 in bridging positions between rhenium atoms. All C–Re–C angles are within two standard deviations of 90 or 180°. Average Re–C distance = 1.99 Å with typical individual standard deviation of 0.06 Å; Re–Re = 2.896 (3) Å.

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(12) This compound has been synthesized in our laboratory by Dr. J. K. Hoyano. The X-ray crystal structure done by Professor T. E. Haas shows idealized D_{2h} symmetry, with Re–Re = 3.00 Å and a Re–Si–Re angle of 75°.

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(15) Positional parameters and bond distances and angles for $H_2Re_2(CO)_8$ will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 Sixteenth St., N.W., Washington, D. C. 20036, by referring to code number JACS-72-6232. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche.

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A Molecular Orbital Model for the Photochemistry of β,γ-Unsaturated Ketones

Sir:

Intensive studies of the spectroscopic and photochemical behavior of β,γ-unsaturated ketones have led