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Bonding of Hydrido Ligands in Transition Metal–Silyl Complexes: Terminal or Bridging? 2. Structure of Bis(μ-diethylsilicon)-(tricarbonyldihydridorhenium)(tetracarbonylrhenium)(*Re–Re*), $Re_2(CO)_7H_2(Si(C_2H_5)_2)_2$

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The structure of $Re_2(CO)_7H_2(Si(C_2H_5)_2)_2$ has been determined crystallographically and consists of two molecules of the complex in the unit cell. The space group is $P\bar{1}$ and the cell parameters are $a = 8.664$ (1) Å, $b = 14.066$ (2) Å, $c = 9.343$ (1) Å, $\alpha = 96.57$ (2)°, $\beta = 93.86$ (1)°, $\gamma = 91.63$ (1)°, and $V = 1127.8$ Å^3. Observed and calculated densities are 2.21 (2) and 2.19 g cm^{-3}, respectively. Based on 2020 independent reflections with $F_o^2 > 3\sigma(F_o^2)$, the data were refined by full-matrix, least-squares techniques to $R = 0.040$ and $R_w = 0.050$. The molecule consists of two bonded rhenium atoms bridged by two diethylsilyl groups. On one rhenium atom is attached three carbonyl groups and two hydrido ligands; the other rhenium atom has four carbonyl groups attached. The Re–Re distance is 3.052 (1) Å, the four Re–Si distances are essentially identical, averaging 2.546 (5) Å, and the Re–Si–Re angles average 73.6 (1)°. The structure is very similar to $Re_2(CO)_8(Si(C_6H_5)_2)_2$, $Re_2(CO)_6H_4(Si(C_2H_5)_2)_2$, and $W_2(CO)_8H_2(Si(C_2H_5)_2)_2$ and is discussed in relation to these compounds. All the evidence is consistent with the hydrido ligands occupying normal, terminal coordination sites on the rhenium atom.

Introduction

Previous discussions of the possibility of hydrido ligands bridging third-row metal–silicon bonds have been based on comparisons of metal–silicon bond lengths,[1-5] with the longer W–Si bond lengths in $W_2(CO)_8H_2(Si(C_2H_5)_2)_2$[3] being interpreted as having bridging hydride ligands. Unlike this tungsten complex, which serves as an internal standard for comparison (containing bridged and unbridged metal–silicon bonds), conclusions about the bonding of the hydrido ligands in $Re_2(CO)_8H_2Si(C_6H_5)_2$[1,2] and $Re_2(CO)_6H_4(Si(C_2H_5)_2)_2$[4] are based on comparisons with $Re_2(CO)_8(Si(C_6H_5)_2)_2$,[5] the only member of the rhenium series containing Re–Si bonds with no adjacent hydride ligands. However, the structure of $Re_2(CO)_8(Si(C_6H_5)_2)_2$ was found to be disordered[6] and thus is not dependable as a standard for unbridged ReSi bonds. The present complex, $Re_2(CO)_7H_2(Si(C_2H_5)_2)_2$, however, is extremely useful in this regard, being analogous to the tungsten complex with two Re–Si bonds adjacent to and two remote from hydride ligands. The structure of this rhenium complex was therefore undertaken because it fulfilled the condition of being an internal standard with respect to the Re–Si bond lengths and therefore removes any ambiguity associated with previous comparisons with $Re_2(CO)_8(Si(C_6H_5)_2)_2$.

Experimental Section

The sample of $Re_2(CO)_7H_2(Si(C_2H_5)_2)_2$, supplied by Drs. W. A. G. Graham and J. K. Hoyano, was sublimed in a sealed tube to give crystals that were suitable for a single-crystal diffraction study. The crystals produced were clear colorless plates. Preliminary photographs showed $\bar{1}$ Lauê symmetry and no systematic absences, consistent with the triclinic space groups $P1$ and $P\bar{1}$. Precise lattice parameters were obtained at 22 °C from the 2θ angles of 17 reflections centered on a Picker manual, four-circle diffractometer using Cu Kα_1 x-radiation (λ 1.54051 Å). The parameters are $a = 8.664$ (1) Å, $b = 14.066$ (2) Å, $c = 9.343$ (1) Å, $\alpha = 96.57$ (2)°, $\beta = 93.86$ (1)°, and $\gamma = 91.63$ (1)°. A Delaunay reduction[7] showed no higher symmetry. The experimental density (2.21 (2) g cm^{-3}), determined by flotation in aqueous Clerici's solution, is in acceptable agreement with that calculated (2.19 g cm^{-3}) assuming two molecules of molecular weight 742.9 amu in a unit cell of volume 1127.8 Å^3.

Intensity data were collected on the Picker manual diffractometer using Cu Kα x-radiation monochromated using the (002) reflecting plane of an oriented graphite crystal and using a 2° takeoff angle. The crystal was aligned with its a^* axis coincident with the ϕ axis of the diffractometer. The crystal faces were identified and the perpendicular distances between parallel faces of the same form measured as {100}, 7.7 × 10^{-2} mm; {010}, 5.3 × 10^{-2} mm; and {001}, 1.9 × 10^{-2} mm. A coupled $\theta/2\theta$ scan technique was used with a 2θ scan speed of 2°/min to collect all reflections with $2\theta \leq 125°$. Initially a peak scan of 90 s (3°) and a stationary background count of 20 s at the limits of the scan were used; however, as the crystal decomposed and the mosaic spread increased, this was changed to 100-s peak scans and 20-s backgrounds. A scintillation counter in conjunction with a pulse height analyzer, tuned to accept 90% of the Cu Kα peak, was used to detect the scattered x rays. Nine well-distributed standard reflections were monitored at approximately 10-h intervals to assess decomposition effects. The data were reduced to structure factor amplitudes by correction for Lorentz, polarization, decomposition, and absorption effects. The decomposition was approximately linear with time and no significant $(\sin\theta)/\lambda$ dependence was observed. Total decomposition for the data collection was about 13%. The 2836

Table II. Fractional Coordinates[a]

Atom	x	y	z
Re(1)	0.02212 (8)	0.16212 (5)	0.20948 (7)
Re(2)	0.19138 (8)	0.35578 (5)	0.29300 (7)
Si(1)	0.2768 (5)	0.1950 (3)	0.3623 (5)
Si(2)	−0.0608 (5)	0.3230 (3)	0.1359 (5)
C(1)	0.143 (2)	0.141 (1)	0.040 (2)
C(2)	−0.166 (2)	0.123 (1)	0.093 (2)
C(3)	0.054 (2)	0.037 (1)	0.266 (2)
C(4)	−0.092 (2)	0.187 (1)	0.381 (2)
C(5)	0.309 (2)	0.342 (1)	0.117 (2)
C(6)	0.303 (2)	0.479 (2)	0.351 (2)
C(7)	0.078 (2)	0.378 (1)	0.470 (2)
C(8)	0.460 (2)	0.147 (1)	0.284 (2)
C(9)	0.273 (2)	0.172 (1)	0.560 (2)
C(10)	0.479 (2)	0.040 (1)	0.287 (2)
C(11)	0.426 (2)	0.216 (2)	0.650 (2)
C(12)	−0.057 (2)	0.342 (1)	−0.061 (2)
C(13)	−0.242 (2)	0.369 (1)	0.208 (2)
C(14)	−0.198 (2)	0.292 (2)	−0.157 (2)
C(15)	−0.288 (2)	0.469 (2)	0.169 (2)
O(1)	0.212 (2)	0.130 (1)	−0.059 (1)
O(2)	−0.281 (2)	0.097 (1)	0.027 (1)
O(3)	0.081 (2)	−0.041 (1)	0.293 (2)
O(4)	−0.164 (2)	0.199 (1)	0.482 (1)
O(5)	0.378 (1)	0.336 (1)	0.019 (1)
O(6)	0.362 (2)	0.550 (1)	0.393 (2)
O(7)	0.015 (2)	0.394 (1)	0.574 (1)

[a] Here and elsewhere standard deviations in parentheses refer to the last digit quoted.

unique reflections collected were reduced to 2020 significant reflections using the criterion that a peak was significantly above background for $F_o^2 \geq 3\sigma(F_o^2)$. Standard deviations, $\sigma(F)$, in the structure factors were computed as described previously[8] using a "p factor" of 0.03.

The high linear absorption coefficient of 212.8 cm^{-1} for Cu Kα x radiation and the platey habit of the crystals gave rise to a considerable range of transmission factors (0.14–0.47). The absorption correction was verified experimentally by investigation of the behavior of F^2_{h00} as a function of ϕ. The internal consistency of the corrected intensities showed maximum deviations of less than 10% from the mean and was considered acceptable.

Solution and Refinement of Structure. The structure was refined[9] by full-matrix, least-squares techniques, minimizing the function $\sum w(|F_o| - |F_c|)^2$, where $|F_o|$, $|F_c|$, and w have been defined previously.[4] The agreement indices are defined as $R = \sum||F_o| - |F_c||/\sum|F_o|$ and $R_w = (\sum w(|F_o| - |F_c|)^2/\sum wF_o^2)^{1/2}$. Atomic scattering factors compiled by Cromer and Mann[10] were used for all nonhydrogen atoms. Anomalous dispersion terms of Cromer[11] for Re and Si were applied to F_c.

The rhenium and silicon atom positions were obtained from a Patterson synthesis. A difference Fourier synthesis phased on the Re and Si positions allowed the location of all other nonhydrogen atoms. The final model in which all nonhydrogen atoms were refined anisotropically converged to $R = 0.040$ and $R_w = 0.050$. The highest features in the final electron density difference map were approximately 1.1 e Å^{-3}, in the vicinity of the rhenium atoms. These peaks could not be interpreted simply as hydride ligand positions. They more likely reflect errors in the absorption correction and inadequate description of the rhenium scattering. Similarly the hydrogen atoms on the ethyl groups could not be located unambiguously.

In the final least-squares cycle 235 parameters were varied, and the error in an observation of unit weight was 1.59 electrons.

The final values of $10|F_o|$ and $10|F_c|$, in electrons, are shown in Table I.[12] The final positional parameters are given in Table II, and the anisotropic thermal parameters (U's) are given in Table III. Standard deviations are estimated from the inverse matrix obtained from the last refinement.

Description of Structure

$Re_2(CO)_7H_2(Si(C_2H_5)_2)_2$ cystallizes with two molecules in the cell, with no unusual nonbonded contacts. A three-dimensional view of the molecule, showing the numbering scheme used, is shown in Figure 1. The molecule has approximate C_s symmetry and has a central framework which is similar to $Re_2(CO)_8(Si(C_6H_5)_2)_2$[5] and $Re_2(CO)_6H_4(Si(C_2H_5)_2)_2$,[4] being composed of a Re–Re bond bridged by two disubstituted silyl groups. In fact, the present complex is actually a composite of the above two complexes with the coordination about Re(1) being similar to the Re atom coordinations in $Re_2(CO)_8(Si(C_6H_5)_2)_2$ and that about Re(2) similar to that in $Re_2(CO)_6H_4(Si(C_2H_5)_2)_2$.

The Re–C(carbonyl) and C–O distances (see Table IV) are normal, agreeing with other such determinations.[1,2,4,5,14–17] There is no significant difference between the carbonyl groups which are mutually trans and the others, which are trans to Re–Re and Re–Si bonds. All carbonyl ligands are essentially linear. The Si–C and C–C (ethyl) distances are normal, agreeing with the sums of the Si and C covalent radii and with

Table III. Thermal Parameters (Å^2)

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}	B^a
Re(1)	0.0497 (5)	0.0456 (5)	0.0432 (5)	−0.0010 (4)	−0.0004 (3)	0.0031 (4)	3.67
Re(2)	0.0448 (5)	0.0436 (5)	0.0483 (4)	0.0010 (4)	−0.0038 (4)	0.0039 (4)	3.63
Si(1)	0.0585 (30)	0.0501 (26)	0.0519 (26)	0.0069 (23)	−0.0042 (21)	0.0098 (21)	4.22
Si(2)	0.0512 (28)	0.0553 (27)	0.0483 (25)	−0.0024 (23)	−0.0051 (21)	0.0101 (21)	4.09
C(1)	0.070 (13)	0.058 (11)	0.071 (14)	0.003 (10)	0.014 (11)	−0.013 (11)	5.33
C(2)	0.076 (13)	0.056 (10)	0.040 (10)	−0.017 (9)	0.005 (9)	−0.012 (8)	4.68
C(3)	0.087 (14)	0.053 (11)	0.051 (11)	−0.017 (10)	−0.020 (10)	0.008 (9)	5.13
C(4)	0.055 (12)	0.060 (11)	0.059 (13)	0.009 (9)	0.006 (10)	0.001 (10)	4.58
C(5)	0.050 (10)	0.054 (10)	0.051 (9)	−0.008 (8)	−0.005 (8)	0.014 (8)	4.08
C(6)	0.038 (10)	0.096 (15)	0.067 (12)	0.001 (10)	−0.014 (8)	0.001 (11)	5.39
C(7)	0.074 (12)	0.051 (11)	0.052 (10)	0.003 (9)	−0.001 (9)	0.006 (8)	4.68
C(8)	0.057 (12)	0.075 (12)	0.082 (14)	0.021 (10)	0.012 (10)	0.019 (10)	5.50
C(9)	0.083 (13)	0.077 (12)	0.044 (10)	−0.004 (11)	−0.010 (9)	0.015 (9)	5.40
C(10)	0.091 (15)	0.065 (13)	0.111 (15)	0.027 (11)	0.011 (12)	0.025 (12)	6.88
C(11)	0.092 (15)	0.111 (17)	0.069 (13)	−0.014 (13)	−0.033 (11)	0.019 (12)	7.28
C(12)	0.091 (14)	0.067 (12)	0.049 (10)	−0.012 (11)	−0.003 (9)	0.008 (8)	5.50
C(13)	0.054 (11)	0.065 (12)	0.089 (13)	0.011 (9)	0.000 (9)	0.008 (10)	5.48
C(14)	0.095 (15)	0.101 (15)	0.057 (11)	−0.026 (13)	−0.023 (10)	0.019 (11)	6.75
C(15)	0.066 (13)	0.060 (12)	0.115 (16)	0.021 (10)	0.004 (11)	−0.000 (11)	6.38
O(1)	0.111 (12)	0.099 (11)	0.074 (10)	−0.009 (9)	0.033 (9)	−0.012 (8)	7.52
O(2)	0.084 (10)	0.093 (10)	0.074 (9)	−0.015 (9)	−0.009 (8)	−0.011 (9)	6.79
O(3)	0.124 (13)	0.063 (9)	0.120 (11)	0.007 (9)	−0.006 (9)	0.021 (8)	8.06
O(4)	0.089 (11)	0.107 (11)	0.060 (9)	−0.013 (9)	0.008 (8)	0.011 (8)	6.75
O(5)	0.070 (9)	0.101 (10)	0.078 (9)	0.007 (8)	0.021 (7)	0.010 (8)	6.48
O(6)	0.087 (11)	0.069 (9)	0.124 (12)	−0.020 (8)	−0.024 (9)	−0.002 (9)	7.61
O(7)	0.108 (11)	0.085 (10)	0.076 (9)	0.012 (9)	0.031 (8)	−0.018 (7)	7.15

[a] Equivalent isotropic thermal parameter.[13]

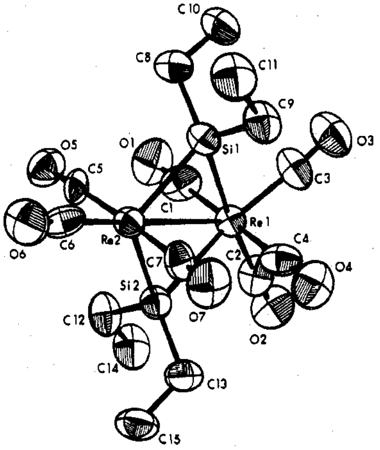

Figure 1. A three-dimensional view of $Re_2(CO)_7H_2(Si(C_2H_5)_2)_2$ showing the numbering scheme used. Thermal ellipsoids are drawn at the 50% probability level.

Table IV. Intramolecular Distances (Å)

Re(1)–Re(2)	3.052 (1)	C(3)–O(3)	1.18 (2)
Re(1)–Si(1)	2.547 (5)	C(4)–O(4)	1.16 (2)
Re(1)–Si(2)	2.548 (5)	C(5)–O(5)	1.12 (2)
Re(2)–Si(1)	2.539 (4)	C(6)–O(6)	1.12 (2)
Re(2)–Si(2)	2.549 (4)	C(7)–O(7)	1.15 (2)
Re(1)–C(1)	1.96 (2)	Si(1)–C(8)	1.90 (2)
Re(1)–C(2)	1.93 (2)	Si(1)–C(9)	1.91 (2)
Re(1)–C(3)	1.92 (2)	Si(2)–C(12)	1.89 (2)
Re(1)–C(4)	1.94 (2)	Si(2)–C(13)	1.85 (2)
Re(2)–C(5)	1.98 (2)	C(8)–C(10)	1.53 (2)
Re(2)–C(6)	1.97 (2)	C(9)–C(11)	1.59 (2)
Re(2)–C(7)	1.98 (2)	C(12)–C(14)	1.56 (2)
C(1)–O(1)	1.13 (2)	C(13)–C(15)	1.54 (2)
C(2)–O(2)	1.15 (2)		

Table V. Intramolecular Angles (deg)

Si(1)–Re(1)–Re(2)	53.0 (1)	Re(1)–Re(2)–C(6)	178.6 (5)
Si(2)–Re(1)–Re(2)	53.2 (1)	Re(1)–C(1)–O(1)	179 (2)
Si(1)–Re(2)–Re(1)	53.3 (1)	Re(1)–C(2)–O(2)	178 (2)
Si(2)–Re(2)–Re(1)	53.2 (1)	Re(1)–C(3)–O(3)	175 (2)
Re(2)–Si(1)–Re(1)	73.7 (1)	Re(1)–C(4)–O(4)	178 (2)
Re(2)–Si(2)–Re(1)	73.5 (1)	Re(2)–C(5)–O(5)	178 (2)
Si(1)–Re(1)–C(3)	80.4 (5)	Re(2)–C(6)–O(6)	175 (2)
Si(2)–Re(1)–C(2)	79.8 (5)	Re(2)–C(7)–O(7)	178 (2)
Si(1)–Re(2)–C(6)	125.5 (5)	C(8)–Si(1)–C(9)	110.4 (8)
Si(2)–Re(2)–C(6)	128.0 (5)	C(12)–Si(2)–C(13)	109.6 (8)
Re(2)–Re(1)–C(1)	89.7 (5)	Si(1)–C(8)–C(10)	115 (1)
Re(2)–Re(1)–C(4)	88.2 (5)	Si(1)–C(9)–C(11)	110 (1)
Re(1)–Re(2)–C(5)	92.4 (5)	Si(2)–C(12)–C(14)	114 (1)
Re(1)–Re(2)–C(7)	91.1 (5)	Si(2)–C(13)–C(15)	116 (1)

other determinations.[3,4,18] Similarly, the Si–C–C and C–Si–C angles (see Table V) are all close to their expected tetrahedral values. The coordination about the Si atoms is then a distorted tetrahedron owing to the acute Re–Si–Re angles of 73.7 (1) and 73.5 (1)°.

Table VI shows some least-squares plane calculations. From plane A we see that the Re_2Si_2 group is planar; the largest deviations from this plane are the silicon atoms (0.02 Å).

The Re(1)–Re(2) distance, at 3.052 (1) Å, is indicative of a Re–Re single bond, being comparable to other such distances[14-16] As in other members of this series,[1,2,4,5] the Re–Re bond is substantiated by the acute Re–Si–Re angles. There is an interesting progression in Re–Re bond lengths through the series $Re_2(CO)_8(Si(C_6H_5)_2)_2$[5] (3.001 (1) Å), $Re_2(CO)_7H_2(Si(C_2H_5)_2)_2$ (3.052 (1) Å), $Re_2(CO)_6H_4(Si(C_2H_5)_2)_2$[4] (3.084 (1) Å), and $Re_2(CO)_8H_2Si(C_6H_5)_2$[1,2] (3.121 (2) Å). However, the Re–Si bonds in this same series remain essentially constant (see Table VII). In $Re_2(CO)_8H_2Si(C_6H_5)_2$ the longer Re–Re bond reflects the fact that only one silyl bridge is constraining the two rhenium atoms together. Furthermore the two extra eclipsed carbonyl groups in this compound result in greater repulsions between the two halves of the molecule again resulting in a longer Re–Re bond. In the other members of the series, however, the increasing Re–Re bond lengths seem to parallel the replacement of carbonyl groups with hydrido ligands, which are of weaker π-accepting ability. It seems, therefore, that the highest occupied orbitals are π orbitals which are antibonding with respect to the Re–Re bond. Thus the greater the π-accepting ability of the ligands (i.e., the more carbonyl groups) the greater the degree of removal of these antibonding electrons; therefore the shorter the Re–Re bond. The Re–Si bonds must have little π contribution since these bonds are changed little by the substitution pattern of carbonyl and hydrido ligands. The observed Re–Si bond lengths are longer than predicted by the sums of the covalent radii (2.45 Å). Similarly, the Zr–Si bond length (2.813 (2) Å) in $ZrCl(\pi\text{-}C_5H_5)_2Si(C_6H_5)_3$[19] is longer than its predicted value (2.62 Å). In the zirconium complex Zr(IV) is formally d^0 so no back-donation into empty silicon d orbitals can occur, suggesting that only Zr–Si σ bonding is important. In contrast, the Co–Si and Rh–Si distances (2.254 (3) Å and 2.303 (4) Å, respectively) in $Co(SiCl_3)(CO)_4$[20] and $RhHCl(SiCl_3)(PPh_3)_2$[21] are both shorter than the values predicted using the Pauling covalent radii (2.33 and 2.42 Å, respectively). It seems, therefore, that metal–silicon π bonding is present in these latter two complexes and absent or minimal in the zirconium and rhenium complexes.

Table VI. Least-Squares Plane Calculations[a]

(A) Atoms Defining Plane: Re(1), Re(2), Si(1), Si(2)

Equation of Plane

$$-0.5693X + 0.0653Y + 0.8195Z - 1.6898 = 0.0$$

Distances of Atoms from Plane (Å)

Re(1)	0.0029	Re(2)	0.0031
Si(1)	−0.020	Si(2)	−0.020

(B) Atoms Defining Plane: Re(1), Re(2), C(1), C(4), C(5), C(7)

Equation of Plane

$$0.6782X - 0.5229Y + 0.5163Z + 0.0354 = 0.0$$

Distances of Atoms from Plane (Å)

Re(1)	0.0004	Re(2)	0.0004
C(1)	0.049	C(4)	−0.029
C(5)	−0.049	C(7)	0.016

[a] *X*, *Y*, and *Z* are orthogonal coordinates (Å) with *X* along the *a* axis, *Y* in the (*a*, *b*) plane, and *Z* along the *c** axis.

Table VII. Relevant Bond Lengths and Angles in Some Transition Metal, Silyl-Bridged Complexes

(a) Bond Lengths, Å

Compd	M–Si	M–M	Ref
$W_2(CO)_8H_2(Si(C_2H_5)_2)_2$	2.586 (5), 2.703 (4)	3.183 (1)	3
$Re_2(CO)_8H_2Si(C_6H_5)_2$	2.544 (9)	3.121 (2)	1, 2
$Re_2(CO)_8(Si(C_6H_5)_2)_2$	2.542 (3)	3.001 (1)	5
$Re_2(CO)_6H_4(Si(C_2H_5)_2)_2$	2.534 (3), 2.536 (3)	3.084 (1)	4
$Re_2(CO)_7H_2(Si(C_2H_5)_2)_2$	2.547 (5), 2.548 (5), 2.539 (4), 2.549 (4)	3.052 (1)	This work

(b) Angles, Deg

Compd	Si–M–M	M–Si–M	Si–M–C
$W_2(CO)_8H_2(Si(C_2H_5)_2)_2$	53.02 (10)	73.97 (12)	109.1 (5)
$Re_2(CO)_8H_2Si(C_6H_5)_2$	53.9 (1)	72.3 (1)	124.8 (13)
$Re_2(CO)_8(Si(C_6H_5)_2)_2$	52.2 (2)	75.7 (3)	78.7 (2)
$Re_2(CO)_6H_4(Si(C_2H_5)_2)_2$	52.55 (6)	74.95 (7)	127.5 (3)
$Re_2(CO)_7H_2(Si(C_2H_5)_2)_2$	53.2 (1)	73.6 (1)	126.8 (5)

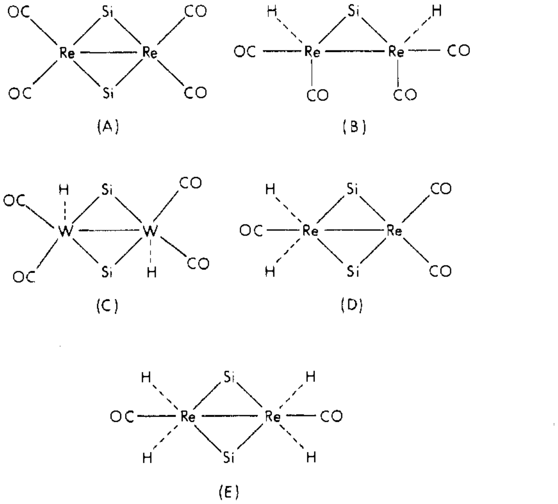

Figure 2. Central cores of the silyl-bridged metal hydrides showing the environments of the hydride ligands.

This is, of course, in agreement with the essentially constant Re–Si distances in the silyl-bridged series. Any explanation of bond shortening resulting from π bonding must be approached cautiously, however, since it is difficult to separate π effects from a σ-inductive effect. Thus the changes in metal–silicon distances in the series $MnH(\pi\text{-}C_5H_5)(CO)_2(Si(C_6H_5)_3)$[22] (2.424 (2) Å) and $MnH(\pi\text{-}C_5H_5)(CO)_2(SiCl_2(C_6H_5))$[23] (2.310 (2) Å) and also the series $Co(SiH_3)(CO)_4$[24] (2.381 (7) Å), $Co(SiCl_3)(CO)_4$[20] (2.254 (3) Å), and $Co(SiF_3)(CO)_4$[25] (2.226 (5) Å) can be attributed to shrinkage of the silicon orbitals by the more electronegative substituents, thereby shortening the metal–silicon bonds.

However uncertain the mode of bonding between the rhenium and silicon atoms in this silyl-bridged, rhenium–rhenium bonded series, it is still possible to compare the distances within the series since all substituents on the silyl groups are similar. Thus the most interesting feature in $Re_2(CO)_7H_2(Si(C_2H_5)_2)_2$ is the similarity in all the Re–Si bonds and their similarity to other members of the series. The Re(2)–Si(1) and Re(2)–Si(2) bonds are adjacent to hydride ligands whereas the Re(1)–Si(1) and Re(1)–Si(2) bonds are "hydrogen free". The similarity of these bonds in the two differing environments is unexpected in view of the proposed hydrogen bridging. The evidence is now conclusively against the hydrogen-bridged Re–Si bond in these silyl-bridged complexes, since we would have expected the two Re–Si bonds adjacent to the hydride ligands to be significantly longer than the "hydride-free" Re–Si bonds, the situation observed in $W_2(CO)_8H_2(Si(C_2H_5)_2)_2$.[3]

To explain why the hydride ligands seem to be terminally bound for the rhenium compounds, but bridging in the tungsten complex, it is useful to consider the coordination about the metal atoms, as is shown in Figure 2. In each compound there are two, mutually trans carbonyl groups on each metal, perpendicular to the plane of the drawing. These and the substituents on the silyl groups are omitted for clarity. The hydride ligands, although not located experimentally, are positioned in what are thought to be their aproximate locations.

Viewing the hydride ligand environments in the examples shown, it is obvious that in the tungsten hydride C, the hydride ligand is more crowded than for the rhenium hydrides. The Si–W–C(carbonyl) angle, which encloses the hydride ligand, is 109.1 (5)° in the tungsten hydride, compared to the analogous angles of 124.8 (13), 126.8 (5), and 127.5 (3)° in the rhenium hydrides, B, D, and E, respectively. It has been shown[22,23,26] that a normal, nonbonded H–C(carbonyl) contact can be as low as 2.0 Å. For a Re–H distance[27] of 1.68 Å calculations show that in the rhenium hydrides, maintaining the minimum C–H contact, a H–Si contact of greater than 2.2 Å arises. However, the situation is much different for $W_2(CO)_8H_2(Si(C_2H_5)_2)_2$. If no hydrogen bridging concept is utilized, then using the unbridged W–Si distance of 2.586 (5) Å and maintaining the minimum C–H contact, a very short Si–H contact of ca. 1.72 Å occurs (this calculated assuming a W–H distance[28] of 1.70 Å). Even using the larger W–Si distance, a short Si–H contact of 1.81 Å arises. Therefore the hydrogen ligands are constrained to be considerably closer to the silicon atoms in the tungsten compound. It is believed that the crowding of the hydrogen by the carbonyl group is then responsible for the appearance of the three-center W–H–Si bond, since it is possible that the three-center bond is favored energetically over a terminal hydride involving the high repulsion energy which must be associated with the very short Si–H nonbonded contacts mentioned.

The nonbonded Si–H contact of 2.2 Å calculated for the rhenium hydrides is believed to be reasonable. In $FeH(\pi\text{-}C_5H_5)(CO)(SiF_2(CH_3))_2$ the hydrogen atom does not seem to be bonded to either silicon atom[29] and is located at 2.06 (7) Å from both silicon atoms. Although seemingly short, these nonbonded contacts can occur, because in these systems the hydrogen atoms approach the silicon atoms in electron density nodes, for example, between the F–Si–F covalent bonds in $FeH(\pi\text{-}C_5H_5)(CO)(SiF_2(CH_3))_2$ or between the C–Si–C bonds in the rhenium hydrides discussed. The repulsion is minimized in these bonding nodes thus facilitating the approach of the hydrogen ligand to the silicon atom.

Although evidence obtained from the structural investigations of $Re_2(CO)_6H_4(Si(C_2H_5)_2)_2$ and $Re_2(CO)_7H_2(Si(C_2H_5)_2)_2$ combined with that obtained from $W_2(CO)_8H_2(Si(C_2H_5)_2)_2$ and $Re(CO)_8(Si(C_2H_5)_2)_2$ exclude the possibility of a three-center Re–H–Si bond, it does not exclude the existence of weak attractive interaction of the hydride ligand with the silicon atom. An insight into this possibility is gained from the structural investigations of $MnH(\pi\text{-}C_5H_5)(CO)_2(Si(C_6H_5)_3)$,[22] $MnH(\pi\text{-}C_5H_5)(CO)_2(SiCl_2(C_6H_5))$,[23] and $FeH(CO)_4(Si(C_6H_5)_3)$,[28] in which the hydride ligands were located experimentally. In both manganese compounds the hydrogen atoms were located at 1.55 (4) and 1.49 (6) Å, respectively, from the manganese atoms and 1.76 (4) and 1.79 (6) Å, respectively, from the silicon atoms. However, in the iron compound the hydrogen atom is 1.64 (10) Å from the iron atom and 2.73 (10) Å from the silicon atom. In the two manganese hydrides the hydride ligands are constrained to be close to the silicon atoms due to steric crowding, the hydrogen atom being only 2.08 (4) Å from the carbonyl ligand in $MnH(\pi\text{-}C_5H_5)(CO)_2(Si(C_6H_5)_3)$ and 1.98 (6) Å from the carbonyl ligand in $MnH(\pi\text{-}C_5H_5)(CO)_2SiCl_2(C_6H_5)$. There is no possibility of increasing the H–Si distance without increasing the hydrogen contact with the carbonyl groups. However, in $FeH(CO)_4(Si(C_6H_5)_3)$ the hydrogen atom is not constrained to be close to the silicon atom, since it is in a sterically less crowded environment than the maganese hydrides. Thus the long Si–H contact observed is indicative of a terminally bound hydride ligand with no attraction to the silicon atom. We believe, therefore, that there is no inherent stability of the bridged hydride ligand in preference to a simple terminal hydride ligand in this series; the close Si–H contacts arise solely as a result of steric crowding by other ligands.

Conclusions

In this series of transition metal–silyl complexes the hydride ligands are bound terminally to the transition metals in *all* the rhenium–hydrido complexes. Only in the manganese and tungsten complexes do the hydride ligands approach closely the silicon atoms. This occurs not as a result of any unusual attraction between the silicon and hydrogen atoms, or due to any inherent differences in properties of the manganese or tungsten complexes with regard to the rhenium analogues, but results from steric crowding which forces the hydride ligands close to the silicon atoms. Thus, we believe that in $Re_2(CO)_8H_2Si(C_6H_5)_2$, $Re_2(CO)_6H_4(Si(C_2H_5)_2)_2$, and $Re_2(CO)_7H_2(Si(C_2H_5)_2)_2$ *the hydride ligands are bonded terminally to the rhenium atoms with no attractive interactions with the silicon atoms.*

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Registry No. $Re_2(CO)_7H_2(Si(C_2H_5)_2)_2$, 63301-80-4.

Supplementary Material Available: Table I, listing the observed and calculated structure amplitudes (9 pages). Ordering information is given on any current masthead page.

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Structural Studies of Steric Effects in Phosphine Complexes. Synthesis and Crystal and Molecular Structure of the Dinitrato(tricyclohexylphosphine)mercury(II) Dimer

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The synthesis and crystal and molecular structure of the dinitrato(tricyclohexylphosphine)mercury(II) dimer is reported. The compound $[Hg(PCy_3)(NO_3)_2]_2$ belongs to the monoclinic space group $P2_1/c$ (C^5_{2h}, No. 14) with $a = 11.143$ (2) Å, $b = 17.956$ (2) Å, $c = 11.756(1)$ Å, and $\beta = 105.98$ (1)° and with two centrosymmetric dimers in the unit cell. The structure was refined anisotropically to final discrepancy indices of $R_F = 0.032$ and $R_{wF} = 0.037$ for 2105 independent reflections measured by diffractometer. In the dimeric molecule the unique mercury atom is coordinated to phosphorus (Hg–P 2.359 (2) Å), to a bidentate nitrato group (Hg–O 2.150 (10), 2.728 (12) Å), and to a monodentate nitrato group (Hg–O 2.504 (9) Å) which forms a bridge to the other centrosymmetrically related mercury atom (Hg–O 2.477 (8) Å). The mercury coordination is distorted square pyramidal with a bridging oxygen atom O(11′) in the apical position and the mercury atom is 0.26 Å above the basal plane. The torsion angles Hg–P–C–H (95°, 65°, 172°) for the three cyclohexyl rings define their orientation with respect to the Hg–P bond. Cone angle calculations are made for PCy_3 ($\theta = 181$ (1)°) and a "ligand profile" is given for PCy_3 in $[Hg(PCy_3)(NO_3)_2]_2$.

Structural studies of tertiary phosphine derivatives of various metals are in progress in our laboratories in an attempt to relate steric and electronic properties of the ligands to molecular stereochemistry. The steric influence of bulky tricyclohexyl and tri-*tert*-butyl groups was evident in the crystal structures found for $Cu(PCy_3)_2ClO_4$[1] and $[t\text{-}Bu_3PH][(t\text{-}Bu_3P)NiBr_3]$.[2] Whereas less sterically hindered phosphines such as Et_3P and Ph_3P give 1:1 complexes with mercuric halides that are formulated as halogen-bridged dimers on the basis of infrared studies,[3] bulkier phosphines might be expected to restrict the mercury from adopting a tetrahedral geometry. Thus, from a vibrational study $Hg(PCy_3)(SCN)_2$ was recently suggested[4] to have a trigonal configuration around mercury similar to that found[5] for $Hg(AsPh_3)(SCN)_2$; an x-ray analysis of $Hg(PCy_3)(SCN)_2$ has shown, however, that it is a polymer with trigonal-pyramidal coordination at mercury.[6] In an investigation of complexes of the type $Hg(PR_3)X_2$, where R is cyclohexyl, *o*-tolyl, or *tert*-butyl, we have synthesized a complex with empirical formula $Hg(PCy_3)(NO_3)_2$, for which vibrational spectra suggest that two types of coordinated nitrato