and C(7) for ring 1 (or plane A) and C(6) for ring 2 or (plane B), show smaller displacements from the respective least-squares planes.

In all three of the 2-biphenylyltellurium trihalide structures investigated, short Te–C(12) intramolecular contacts have been observed. These are 2.945 (9) Å in the tribromide, 3.32 (1) Å in the α triiodide and 3.18(1) Å in the β triiodide. These distances may be compared with the shortest packing distances of 3.83 and 3.84 Å observed between Te and aromatic carbon atoms in dibenzotellurophene.[8] The significance of these short Te–C(12) contacts with respect to conversion of the 2-biphenylyltellurium trihalides to dibenzotellurophene dihalides has been discussed.[1]

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Registry No. β-$C_{12}H_9TeI_3$, 55776-30-2.

Supplementary Material Available: Table IV, the calculated (idealized) positions and assigned isotropic thermal parameters of the hydrogen atoms, Table V, the root-mean-square amplitudes of vibration, and Table VI, the observed and calculated structure factors (8 pages). Ordering information is given on any current masthead page.

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Bonding of Hydrido Ligands in Transition Metal–Silyl Complexes: Terminal or Bridging? 1. Structure of Bis(μ-diethylsilicon)-bis(tricarbonyldihydridorhenium)(*Re*–*Re*), $Re_2(CO)_6H_4(Si(C_2H_5)_2)_2$

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The structure of $Re_2(CO)_6H_4(Si(C_2H_5)_2)_2$ has been determined crystallographically and consists of one molecule of the complex, with symmetry $\bar{1}$, in the unit cell (space group $P\bar{1}$, reduced cell parameters a = 8.768 (3) Å, b = 8.776 (3) Å, c = 8.357 (3) Å, α = 97.76 (3)°, β = 112.88 (3)°, γ = 109.07 (3)°, and V = 533.9 Å^3). Observed and calculated densities are 2.23 (2) and 2.25 g cm^{-3}, respectively. Based on 1510 independent reflections with $F_o^2 \geq 3\sigma(F_o^2)$, the data were refined by full-matrix, least-squares techniques to R = 0.034 and R_w = 0.045. The central cluster of the molecule consists of two rhenium and two silicon atoms in the shape of a rhombus, with like atoms at opposing corners. A bond joins the two rhenium atoms across the shorter diagonal. One carbonyl group on each rhenium atom lies along the Re–Re axis, while the other four lie above and below the plane of the rhombus, two on each rhenium atom. The ethyl groups are bonded, two on each silicon atom, above and below the rhombus plane giving the silicon atoms distorted tetrahedral environments. The Re–Re bond is 3.084 (1) Å, the two independent Re–Si distances are 2.534 (3) and 2.536 (3) Å, the Re–Re–Si angles average 52.53 (6)° and the Re–Si–Re′ angle is 74.95 (7)°. The hydride ligands are judged to occupy normal terminal positions; thus the rhenium coordination can be described as distorted hexagonal bipyramidal.

Introduction

The reactions of disubstituted silanes with dirhenium decacarbonyl and with both tungsten and molybdenum hexacarbonyls have produced an interesting series of silicon-bridged, metal–metal bonded species.[1,2] A systematic study of representative molecules from this series has been undertaken to elucidate the major structural characteristics of these systems. Ignoring the carbonyl groups, these molecules fall into five major classes: (I) no hydride ligands, e.g., $Re_2(CO)_8(Si(C_6H_5)_2)_2$;[3] (II) two hydride ligands, each on a different transition metal but both adjacent to the same silicon atom, e.g., $Re_2(CO)_8H_2Si(C_6H_5)_2$;[4,5] (III) two hydride ligands, each attached to a different transition metal and adjacent to different silicon atoms, e.g., $W_2(CO)_8H_2(Si(C_2H_5)_2)_2$;[6] (IV) two hydride ligands attached to one transition metal and adjacent to different silicon atoms, e.g., $Re_2(CO)_7H_2(Si(C_2H_5)_2)_2$;[7] (V) four hydride ligands, two attached to each transition metal, with each silicon having two adjacent hydrogen atoms, e.g., $Re_2(CO)_6H_4(Si(C_2H_5)_2)_2$, the topic of this paper. These structural fragments are shown in Figure 1 using valence bond descriptions and normal terminal transition metal hydride formulation, with the exceptions of IIIb where bridging hydrogen atoms are indicated and IIIc where the terminal hydrogen atoms interact weakly with the silicon atoms. Our interest in this series has centered around the central cluster of transition metal and silicon atoms and hydride ligands to obtain information concerning the nature of the bonding of the hydride ligands.

It had been suggested, on the basis of spectroscopic evidence, that in these compounds the hydride ligands bridged the metal–silicon bonds rather than being bonded terminally to the metals.[1,4,5] The basis of this argument was the spectroscopic studies of Kaesz and co-workers[8,9] on the trimeric rhenium hydride $(HRe(CO)_4)_3$ and its deuteride $(DRe(CO)_4)_3$, in which the absence of a distinct metal–hydrogen stretching frequency in the infrared spectra was interpreted as evidence that the hydride ligands were bridging the Re–Re bonds. Since the terminal metal–hydrogen stretch should be visible in the infrared spectrum, its absence was postulated as a characteristic feature of M–H–M bridges. This postulate was extended to the series of transition metal–silicon hydrides where the metal–hydrogen stretch was again absent in the infrared spectra,[2] and consequently a M–H–Si bridge was postulated. In addition, in $Re_2(CO)_8H_2Si(CH_3)_2$, the methyl resonance

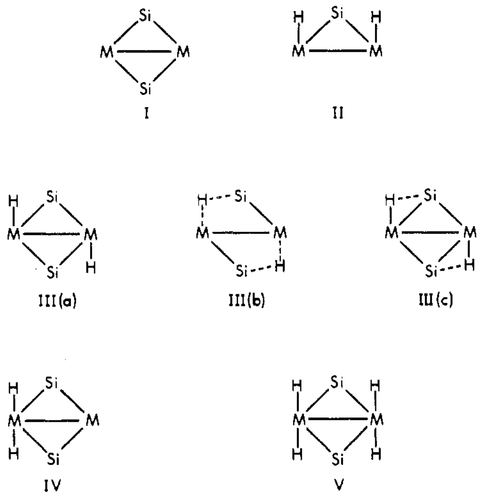

Figure 1. Central frameworks of the silyl-bridged transition metal series.

in the proton NMR spectrum appeared as a 1:2:1 triplet at τ 8.87 with a coupling constant $J = 1.5$ Hz.[2,4] The magnitude of this coupling constant suggested that the high-field protons, which are splitting the methyl resonance, are close to the dimethylsilyl moiety since $J(CH_3\text{–}Si\text{–}H) = 4.2$ Hz for dimethylsilane alone.

The first member of this series to have its molecular structure solved by x-ray techniques was $Re_2(CO)_8H_2Si(C_6H_5)_2$.[4,5] Unfortunately, owing to the dominance of the rhenium scattering, location of the hydride ligands was not possible. However, the coordination sites adjacent to the metal–silicon bonds were conspicuously vacant so the approximate locations of the hydrogen atoms were apparent. Elder postulated[5] that these hydrogen atoms were located in the Re_2Si plane such that the Re–Re–H angle was 90°. Thus for a rhenium–hydrogen bond length[10] of ca. 1.68 Å, a silicon–hydrogen bond length of 1.59 Å would result. This position, he said, would give the proper orientation for a three-center Re–H–Si bond. However, the subsequent structure determination of the nonhydridic species, $Re_2(CO)_8(Si(C_6H_5)_2)_2$,[3] produced Re–Si bond lengths (2.542 (3) Å) which are remarkably similar to those in $Re_2(CO)_8H_2Si(C_6H_5)_2$ (2.544 (9) Å). This is unexpected if a three-center, two-electron Re–H–Si bond is involved in the latter. An unambiguous comparison of the two structures was hindered, however, by the realization that a disorder problem was present in $Re_2(CO)_8(Si(C_6H_5)_2)_2$.[3,11] Although it was not believed that this disorder would affect the bond lengths in the central Re_2Si_2 cluster, it did cast some doubt on accurate comparisons of the two compounds.

Further evidence favoring the three-center M–H–Si bond arose from the structural determination of $W_2(CO)_8H_2(Si(C_2H_5)_2)_2$,[6] (type IIIb in Figure 1) in which two differing tungsten–silicon bonds were found (2.586 (5) and 2.703 (4) Å). The longer W–Si bond was interpreted as being due to hydrogen insertion into this bond, thus forming a three-center W–H–Si bond. The structural determinations of members IV and V ($Re_2(CO)_7H_2(Si(C_2H_5)_2)_2$ and $Re_2(CO)_6H_4(Si(C_2H_5)_2)_2$, respectively) were therefore undertaken to obtain further information concerning the bonding of the hydride ligands in this series. These structural determinations are described in this and the following paper.

Experimental Section

The sample of $Re_2(CO)_6H_4(Si(C_2H_5)_2)_2$, which was kindly supplied by Drs. W. A. G. Graham and J. K. Hoyano, was recrystallized from *n*-hexane, yielding colorless crystals with the shape of a general parallelepiped. Preliminary photography indicated only Lauē symmetry $\bar{1}$ indicative of a triclinic space group. Weissenberg (*0kl*, *1kl*, *2kl*: Cu Kα x radiation) and precession (*h0l*, *h1l*, *h2l*, *hk0*, *hk1*, *hk2*: Mo Kα x radiation) photographs showed no systematic absences, consistent with the space groups $P1$ and $P\bar{1}$. Precise lattice parameters were obtained at 23 °C from an analysis of the setting angles for 18 reflections which had been carefully centered on a Picker manual four-circle diffractometer using Cu Kα_1 radiation of wavelength 1.540 51 Å. The reduced primitive cell[12] has the parameters $a = 8.768$ (3) Å, $b = 8.776$ (3) Å, $c = 8.357$ (3) Å, $\alpha = 97.76$ (3)°, $\beta = 112.88$ (3)°, $\gamma = 109.07$ (3)°, and V = 533.9 Å^3. The cell reduction failed to show the presence of higher symmetry. The observed density (2.23 (2) g cm^{-3}), obtained by flotation in aqueous Clerici's solution (thallous formate-malonate, $\rho_{max} = 4.3$ g cm^{-3}), is in satisfactory agreement with that calculated on the basis of one molecule in the cell (2.25 g cm^{-3}). For space group $P\bar{1}$ the imposed symmetry on the molecule is $\bar{1}$, while no restrictions are necessary for space group $P1$. Since $Re_2(CO)_6H_4(Si(C_2H_5)_2)_2$ can have $\bar{1}$ symmetry, $P\bar{1}$ was chosen and was later verified by successful refinement of the model.

Intensity data were collected on the Picker manual diffractometer using Cu Kα radiation monochromated by the (002) reflecting plane of an oriented graphite crystal using a takeoff angle of 2°. Two crystals were used during data collection and in each case they were aligned with their crystallographic c^* axis coincident with the diffractometer ϕ axis. The dimensions of the two crystals are 0.10 × 0.07 × 0.08 mm and 0.08 × 0.04 × 0.07 mm. Data were collected for reflections with 2θ values between 0 and 125° using a coupled θ–2θ scanning technique, a 2θ scan speed of 2°/min, and a scan width of 3°. Stationary background counts were measured at the limits of each scan for 20 s. The detector was a scintillation counter and was used in conjunction with a pulse height analyzer tuned to accept 90% of the Cu Kα peak. Eight standard reflections, well distributed through reciprocal space, were monitored at approximately 10-h intervals to investigate possible decomposition. The decomposition was found to be approximately linear with time and free of $(\sin\theta)/\lambda$ dependence. Each crystal underwent about 10% decomposition. The data were reduced to structure factor amplitudes by correction for Lorentz, polarization, decomposition, and absorption effects. Of the 1690 unique reflections measured, 1510 were significantly above background using the criterion $F_o^2 \geq 3\sigma(F_o^2)$. Standard deviations, $\sigma(F)$, in the structure factors were computed[13] using a "p factor" of 0.03. The linear absorption coefficient (226.1 cm^{-1}) for Cu Kα radiation resulted in a range of transmission factors of 0.14–0.38. The absorption correction was verified by observation of the variation of F^2_{00l} ($\chi = 90°$) as ϕ was varied. The final corrected intensities of this ϕ scan data showed variation from the mean of less than 10% and was judged to be internally consistent.

Solution and Refinement of Structure. The structure was refined[14] by full-matrix, least-squares techniques, minimizing the function $\sum w(|F_o| - |F_c|)^2$, where $|F_o|$ and $|F_c|$ are the observed and calculated structure amplitudes and the weight w is $1/\sigma^2(F)$. The agreement indicies, R and R_w, 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 by Cromer and Mann[15] were used for all nonhydrogen atoms. Anomalous dispersion terms of Cromer[16] for Re and Si were applied to F_c.

The rhenium and silicon atoms were obtained from a Patterson synthesis. A difference Fourier synthesis phased on these atoms indicated the positions of all other nonhydrogen atoms. The final least-squares cycle, with all nonhydrogen atoms refined anisotropically, converged at $R = 0.034$ and $R_w = 0.045$.

An electron density difference map was calculated in an attempt to locate the hydrogen atoms in the structure, especially those attached to the rhenium atoms. It was encouraging that the highest peaks in the electron density difference map (1.8–1.1 e Å^{-3}) were located in the spaces between the rhenium and silicon atoms in the approximate positions for hydrogen atoms bound to rhenium. The method of LaPlaca and Ibers[17] was therefore employed in an attempt to discern whether these peaks were hydrogen atoms or merely artifacts arising from improper treatment of the rhenium scattering or vibrations or systematic errors in the data. Ibers reasoned that if a peak is merely an artifact, then as the number of terms in the Fourier series is varied, the peak should disappear or shift markedly. A peak due to a hydrogen atom, however, should remain approximately in the same position and the peak height should decrease as the $(\sin\theta)/\lambda$ limit decreases. Performing Fourier syntheses for $(\sin\theta)/\lambda$ intervals of ca. 0.05 Å^{-1} from 0.20 to 0.58 Å^{-1} (complete data) the peaks in question never varied in position significantly but their intensities were always more than double that calculated by the method of LaPlaca and Ibers. A

Table II. Atomic Positional Parameters

Atom	x	y	z
Re	0.11043 (5)[a]	0.13101 (5)	−0.06349 (5)
Si	−0.1353 (3)	0.1418 (3)	0.0199 (3)
C(1)	0.2435 (15)	0.2953 (14)	−0.1489 (16)
C(2)	0.2969 (15)	0.2565 (13)	0.1896 (16)
C(3)	−0.0765 (15)	0.0090 (13)	−0.3162 (16)
C(4)	−0.0662 (15)	0.3140 (13)	0.2282 (15)
C(5)	−0.2010 (20)	0.2785 (16)	0.3087 (19)
C(6)	−0.3501 (14)	0.1276 (13)	−0.1692 (16)
C(7)	−0.3295 (19)	0.2802 (16)	−0.2393 (20)
O(1)	0.3188 (16)	0.3889 (13)	−0.2041 (16)
O(2)	0.4137 (12)	0.3383 (11)	0.3362 (11)
O(3)	−0.1842 (13)	−0.0596 (13)	−0.4691 (11)

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

representation of the electron density difference map, calculated through the plane of the rhenium and silicon atoms, for a $(\sin\theta)/\lambda$ limit of 0.35 is shown in Figure 2. The hydrogen atoms can be located anywhere within the 0.4 e Å^{-3} contour and thus cannot be located with certainty. This implies that the peaks are receiving contributions from the hydrogen scattering and also from artifacts arising from an inadequate description of the rhenium scattering and residual absorption effects. In addition, doubt concerning the validity of these peaks resulted from our failure to locate the hydrogen atoms of the ethyl groups. Subsequent attempts to refine the hydride positional and thermal parameters failed.

In the final least-squares cycle, in which $R = 0.034$ and $R_w = 0.045$, 110 parameters were varied, and the error in an observation of unit weight was 1.61 electrons.

The final values of $10|F_o|$ and $10|F_c|$, in electrons, are shown in Table I.[18] The final positional and anisotropic thermal parameters are shown in Tables II and III, respectively. Standard deviations are estimated from the inverse matrix obtained from the last refinement.

Description of Structure

$Re_2(CO)_6H_4(Si(C_2H_5)_2)_2$ crystallizes with one molecule in the cell and has imposed site symmetry $\bar{1}$. There are no unusual intermolecular contacts, the shortest being comparable to the sums of the van der Waals radii. A three-dimensional view of the molecule, showing the numbering scheme, is shown in Figure 3.

The molecule has approximate C_{2h} symmetry and is composed of a central cluster of two rhenium and two silicon atoms in the shape of a rhombus. Like atoms occupy opposing corners with a bond joining the two rhenium atoms across the shorter diagonal. One carbonyl group on each rhenium atom is trans to the Re–Re bond, while the other four lie above and below the plane of the rhombus, two mutually trans on each rhenium atom. The ethyl groups are bonded, two on each silicon atom, one above and one below the rhombus plane, giving the silicon atoms distorted tetrahedral environments.

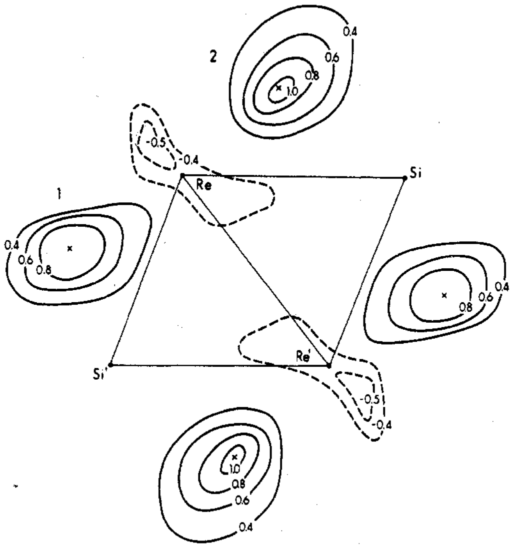

Figure 2. Electron density difference map through the Re_2Si_2 plane. The $(\sin\theta)/\lambda$ cutoff is 0.35 Å^{-1}. Contours are drawn in e Å^{-3}.

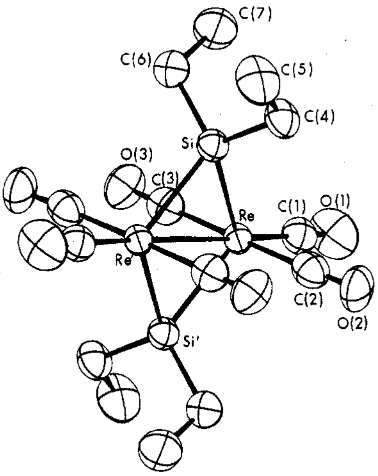

Figure 3. A three-dimensional view of $Re_2(CO)_6H_4(Si(C_2H_5)_2)_2$ showing the numbering scheme used. Thermal ellipsoids are drawn at the 50% probability level.

The Re–Re′ distance, at 3.084 (1) Å (see Table IV), is indicative of a Re–Re single bond and can be compared with other such distances in $Re_2(CO)_{10}$,[20] 3.02 Å; $[Re_4(CO)_{16}{}^{2-}]$,[21] 2.956 (7)–3.024 (7) Å; $[H_2Re_3(CO)_{12}{}^{-}]$[22], 3.035 (7) Å (unbridged Re–Re bond); $Re_2(CO)_8(Si(C_6H_5)_2)_2$[3], 3.001 (1) Å; and $Re_2(CO)_8H_2Si(C_6H_5)_2$,[4,5] 3.121 (2) Å. The presence of a Re–Re bond is further substantiated by the acute Re–Si–Re′ angle of 74.95 (7)°. It has been noted previously[23-27] that for groups (B) bridging two metal atoms, the M–B–M angle is constrained to be acute when an M–M bond is present. However, when no M–M bond is involved the M–B–M angle is much larger. In this case we would expect the Re–Si–Re′

Table III. Thermal Parameters (Å^2)

Atom	U_{11}[a]	U_{22}	U_{23}	U_{12}	U_{13}	U_{23}	B[b]
Re	0.0389 (3)	0.0331 (3)	0.0418 (3)	0.0125 (2)	0.0216 (2)	0.0096 (2)	2.99
Si	0.041 (1)	0.038 (1)	0.050 (1)	0.017 (1)	0.023 (1)	0.010 (1)	3.37
C(1)	0.054 (6)	0.048 (6)	0.067 (7)	0.023 (5)	0.031 (5)	0.011 (5)	4.36
C(2)	0.054 (6)	0.054 (6)	0.074 (7)	0.029 (5)	0.037 (6)	0.026 (5)	4.39
C(3)	0.059 (6)	0.054 (6)	0.065 (7)	0.023 (5)	0.039 (6)	0.025 (5)	4.35
C(4)	0.065 (7)	0.045 (6)	0.063 (6)	0.021 (5)	0.036 (5)	0.006 (5)	4.53
C(5)	0.095 (10)	0.068 (8)	0.095 (10)	0.025 (7)	0.071 (9)	0.010 (7)	6.38
C(6)	0.045 (6)	0.046 (5)	0.074 (7)	0.015 (5)	0.025 (5)	0.019 (5)	4.49
C(7)	0.074 (8)	0.069 (8)	0.093 (9)	0.032 (7)	0.020 (7)	0.041 (7)	6.50
O(1)	0.107 (8)	0.076 (6)	0.119 (8)	0.032 (6)	0.079 (7)	0.047 (6)	7.19
O(2)	0.065 (5)	0.063 (5)	0.054 (5)	0.007 (4)	0.006 (4)	0.000 (4)	5.99
O(3)	0.075 (6)	0.095 (6)	0.044 (4)	0.009 (5)	0.020 (4)	0.010 (4)	6.53

[a] The form of the thermal ellipsoid is $\exp[-2\pi^2(a^{*2}U_{11}h^2 + b^{*2}U_{22}k^2 + c^{*2}U_{33}l^2 + 2a^*b^*U_{12}hk + 2a^*c^*U_{13}hl + 2b^*c^*U_{23}kl)]$.[18]
[b] Equivalent isotropic thermal parameter.

Table IV. Intramolecular Distances (Å) and Angles (deg)[a]

	Distances		
Re–Re′[a]	3.084 (1)	Si–C(6)	1.88 (1)
Re–Si	2.534 (3)	C(1)–O(1)	1.14 (1)
Re–Si′	2.536 (3)	C(2)–O(2)	1.17 (1)
Re–C(1)	1.94 (1)	C(3)–O(3)	1.17 (1)
Re–C(2)	1.97 (1)	C(4)–C(5)	1.54 (2)
Re–C(3)	1.96 (1)	C(6)–C(7)	1.52 (2)
Si–C(4)	1.89 (1)		
	Angles		
Re′–Re–C(1)[a]	178.5 (3)	C(3)–Re–C(2)	179.1 (4)
Re′–Re–C(2)	91.0 (3)	C(4)–Si–C(6)	108.5 (5)
Re′–Re–C(3)	89.3 (3)	Re–Si–Re′	74.95 (7)
Re′–Re–Si	52.55 (6)	Re–C(1)–O(1)	178.0 (10)
Re′–Re–Si′	52.50 (6)	Re–C(2)–O(2)	175.7 (10)
C(1)–Re–C(3)	89.4 (4)	Re–C(3)–O(3)	177.5 (10)
C(1)–Re–C(2)	90.2 (5)	Si–C(4)–C(5)	114.5 (8)
C(1)–Re–Si	126.6 (3)	Si–C(6)–C(7)	115.0 (8)
C(1)–Re–Si′	128.3 (3)		

[a] Primed atoms related by an inversion center.

angle to approximate the tetrahedral angle of a tetrasubstituted silane if no Re–Re bond were involved. The acute M–B–M angles could also result from van der Waals repulsions. For example, in $[Ph_3PCuI]_4$[28] and $[Et_3PCuI]_4$[29] the I atoms bridge the Cu atoms and the Cu–I–Cu angles are ca. 66°, even though there are no Cu–Cu bonds involved. In these tetrameric compounds the acute Cu–I–Cu angles are attributed to van der Waals repulsions between the I atoms.

The Re–C(carbonyl) and C–O distances average 1.96 (2)[30] and 1.16 (2) Å, respectively, and are normal for such distances, agreeing well with other determinations.[3-5,20-22] There is no significant difference between the Re–C or C–O distances for those carbonyl ligands which are mutually trans and the one which is trans to the Re–Re′ bond. The carbonyl groups are essentially linear with small deviations from linearity probably resulting from packing effects. The Si–C and C–C distances, averaging 1.89 (1) and 1.53 (2) Å, respectively, are close to what one would expect based on the sums of the respective covalent radii and agree with other determinations of transition metal silyl complexes.[6,31] Similarly the C–Si–C and Si–C–C angles are close to the expected tetrahedral values.

The average Re–Si bond length in the present complex (2.535 (3) Å) is similar to the analogous distances in $Re_2(CO)_8H_2Si(C_6H_5)_2$[4,5] and $Re_2(CO)_8(Si(C_6H_5)_2)_2$[3] (2.544 (9) and 2.542 (3) Å, respectively), all of which are significantly longer than the Re–Si distances of 2.49 (1) and 2.509 (5) Å in $ReH(\eta^5\text{-}C_5H_5)(CO)_2Si(C_6H_5)_3$[32] and $HRe_2(CO)_9SiCl_2(C_6H_5)$,[33] respectively, in which the silyl groups are terminally bound to the rhenium atoms. This similarity in Re–Si bonds in the above three silyl-bridged complexes is indeed the most significant result of this study. Based on the postulate that the hydride ligands were bridging the Re–Si bonds we would have expected these bonds in $Re_2(CO)_8H_2Si(C_6H_5)_2$ and $Re_2(CO)_6H_4(Si(C_2H_5)_2)_2$ to differ from those in $Re_2(CO)_8(Si(C_6H_5)_2)_2$ as was observed with the two differing W–Si bonds in $W_2(CO)_8H_2(Si(C_2H_5)_2)_2$.[6]

Although the hydride ligands could not be located in these structures, investigation of the central framework, in particular the metal–silicon bonds, has proved exceedingly valuable in obtaining information about the bonding exhibited by the hydride ligands. Three basic possibilities exist, as shown for $W_2(CO)_8H_2(Si(C_2H_5)_2)_2$ in Figure 1, types IIIa–c: (a) the hydride ligand is terminally bonded to the transition metal with no interaction with the silicon atom; (b) the hydride ligand bridges the transition metal–silicon bond forming a three-center, two-electron bond; (c) the hydride ligand is terminally bonded to the transition metal, but with weak attractive interaction with the silicon atom. In $W_2(CO)_8H_2(Si(C_2H_5)_2)_2$ it is believed that type IIIb bonding is present. This has been inferred from the differences in the W–Si distances (2.586 (5) and 2.703 (4) Å). In all three analogous rhenium complexes, however, the Re–Si bond lengths (2.535 (3), 2.544 (9), and 2.542 (3) Å) are essentially identical suggesting the same type of Re–Si bond in each. Furthermore, these Re–Si distances correspond to the shorter (unbridged) W–Si distance in the tungsten analogue. No longer Re–Si distance, corresponding to the longer (bridged) W–Si distance, has been observed in this series (based on a difference in covalent radii of ca. 0.02 Å between W and Re we would expect a hydride-bridged Re–Si distance of ca. 2.68 Å). The structural evidence now strongly opposes the existence of bridging hydride ligands in the rhenium series, suggesting instead that these hydride ligands are terminally bonded to the rhenium atoms. Furthermore, the Raman spectrum of $Re_2(CO)_8H_2Si(C_6H_5)_2$ is now available[34] and shows a band at 1790 cm^{-1} shifting to 1280 cm^{-1} in the deuteride. The 1790-cm^{-1} value falls well within the region 1900 ± 300 cm^{-1} considered characteristic of terminal M–H absorption.[35] The lack of detectable infrared intensity for these vibrations is unexplained, but other silyl–transition metal hydrides which absorb in the terminal M–H region are also "silent" in the infrared.[36]

We cannot, however, on the evidence thus far presented, make a distinction between terminal hydride ligands with or without weak interactions with the silicon atoms (types IIIa and c). We defer discussion of this aspect and also discussion of the reasons for the differences in the bonding in the W and Re complexes until the following paper.

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Registry No. $Re_2(CO)_6H_4(Si(C_2H_5)_2)_2$, 63301-79-1.

Supplementary Material Available: Table I, listing the observed and calculated structure amplitudes (7 pages). Ordering information is given on any current masthead page.

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