Crystal and Molecular Structure of $W_2(CO)_8H_2\{Si(C_2H_5)_2\}_2$. A Compound Containing a Hydrogen-Bridged Transition Metal–Silicon Bond

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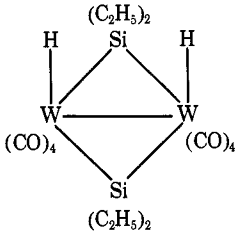
Abstract: The crystal and molecular structure of $W_2(CO)_8H_2\{Si(C_2H_5)_2\}_2$ has been determined by X-ray diffraction techniques. The compound crystallizes in the monoclinic system with space group $P2_1/n$, unit cell dimensions a = 9.212 (1), b = 10.131 (1), c = 12.749 (1) Å, β = 99.07 (1)°, and two molecules per unit cell. The discrepancy between the observed density (2.04 g cm^{-3}) and the calculated density (2.16 g cm^{-3}) is discussed. The structure was refined using least-squares methods to give a conventional R factor 0.038 for 945 significant and independent reflections. Intensities were estimated from counter measurements. The molecule is required to have an inversion center from space group considerations. The structure contains an approximately planar fragment $(CO)_2WSi_2W(CO)_2$, where the two tungsten atoms of the central W_2Si_2 core are held together by a metal–metal bond as well as the two silicon bridges. The WSi_2W fragment forms a parallelogram with two distinctly different W–Si distances of 2.586 (5) and 2.703 (4) Å. This feature is interpreted in terms of hydrogen insertion between the silicon and tungsten atoms involved in the longer pair of distances. The environment of the tungsten atoms can then be crudely described by a pentagonal bipyramid with axial bonds to two carbonyls and the equatorial bonds involving two carbonyls, a silicon atom, the tungsten–tungsten bond, and the two-electron, three-center, W–H–Si bond.

The reactions of partially substituted silanes with transition metal carbonyl derivatives have produced a novel series of silicon–hydrogen–metal compounds. In particular, the reactions of diaryl- or dialkylsilanes with dirhenium decacarbonyl[1] has produced compounds of the stoichiometry $Re_2(CO)_8H_2SiR_2$ (**1**) (R = C_6H_5, CH_3, C_2H_5), $Re_2(CO)_6H_4(SiR_2)_2$ (**2**) (R = CH_3, C_2H_5), and $Re_2(CO)_7H_2(SiR_2)_2$ (**3**) (R = CH_3, C_2H_5). The structure of **1** for R = C_6H_5 has been reported,[2] and on the basis of spectroscopic studies a new type of hydrogen bridge was formulated in that the hydrides, while essentially bound in a terminal fashion to the rhenium atoms, were also weakly bonded directly to the silicon atom. The formation of the postulated silicon–hydrogen bond produces no obvious change in the geometry of the Re_2Si_2 unit, as demonstrated by the structures of the compounds $Re_2(CO)_8\{Si(C_6H_5)_2\}_2$[3] and $Re_2(CO)_6H_4\{Si(C_2H_5)_2\}_2$.[4]

The extension of the photochemical reactions to tungsten hexacarbonyl[1] has produced ditungsten derivatives, albeit indirectly. The formation of the important and isolable products can be represented schematically as follows.

$$W(CO)_6 \xrightarrow[h\nu]{SiH_2R_2} W_2(CO)_{10}(SiR_2)_2 \xrightarrow[h\nu]{SiH_2R_2} W_2(CO)_8H_2(SiR_2)_2$$

The structure of $W_2(CO)_8H_2\{Si(C_2H_5)_2\}_2$ was undertaken to increase our understanding of these systems. The structures that seemed plausible may be represented as I–VI. These structures show the variation from pure terminal hydride, through terminal hydride with a weak silicon–hydrogen bond, to the case with definite insertion of the hydrogen atom into the tungsten–silicon bond. Only those cases where both the tungsten atoms were equivalent and both hydrides equivalent were considered on the grounds of the spectroscopic evidence.[1]



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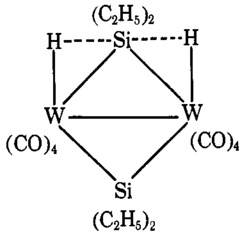

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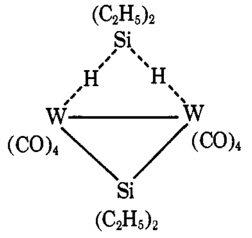

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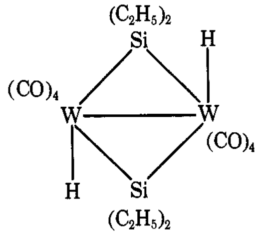

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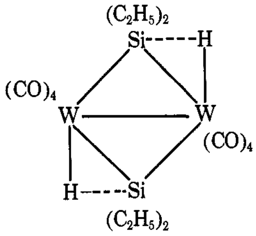

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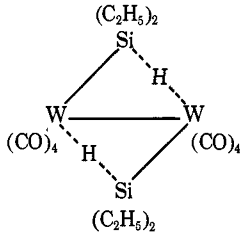

VI

The system was particularly appealing in that if bridging did occur, the unbridged distance would be an internal reference, and hence the comparison would be easier. It should be pointed out that at the time the structure was undertaken the favored description was II and the studies referred to in ref 3 and 4 had not been started.

Experimental Section

Crystals of $W_2(CO)_8H_2\{Si(C_2H_5)_2\}_2$ suitable for a single-crystal X-ray study were obtained by recrystallization from n-hexane of the

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[1] J. K. Hoyano and W. A. G. Graham, *J. Amer. Chem. Soc.*, submitted for publication.

[2] M. Elder, *Inorg. Chem.*, **9**, 762 (1970).

[3] M. J. Bennett and T. E. Haas, manuscript in preparation.

[4] M. J. Bennett and M. Cowie, manuscript in preparation.

Table I. Final Coordinate and Thermal Parameters[a]

Atom	x	y	z	β_{11}[b]	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}	B, Å^2 [c]
W	0.14820 (6)	0.08287 (7)	0.00860 (5)	152.3 (11)	211.6 (12)	118.5 (7)	7.8 (9)	26.0 (6)	17.5 (7)	7.098
Si	0.0938 (5)	−0.1341 (5)	−0.0971 (4)	188.9 (65)	264.1 (73)	130.6 (40)	10.9 (57)	43.5 (41)	−15.7 (45)	8.410
C1	0.229 (2)	−0.021 (2)	0.132 (1)	255 (31)	201 (23)	139 (17)	31 (22)	70 (18)	12 (16)	8.354
C2	0.058 (2)	0.195 (2)	−0.115 (1)	202 (25)	195 (24)	145 (16)	+19 (20)	48 (16)	7 (16)	7.923
C3	0.298 (2)	0.220 (2)	0.054 (1)	216 (30)	257 (32)	147 (17)	4 (23)	4 (19)	−16 (19)	9.182
C4	0.308 (2)	0.030 (2)	−0.071 (2)	146 (24)	262 (28)	183 (19)	−20 (21)	48 (18)	25 (18)	9.042
C5	0.101 (3)	−0.151 (3)	−0.245 (2)	388 (54)	466 (55)	211 (30)	5 (44)	57 (30)	−1 (31)	15.121
C6	0.010 (3)	−0.082 (3)	−0.304 (2)	485 (66)	511 (60)	225 (32)	200 (49)	99 (36)	83 (32)	16.923
C7	0.212 (2)	−0.278 (2)	−0.042 (2)	237 (30)	249 (30)	294 (28)	66 (26)	60 (24)	−72 (24)	12.272
C8	0.139 (3)	−0.413 (2)	−0.076 (2)	449 (60)	325 (41)	275 (33)	83 (40)	67 (33)	−36 (30)	15.236
O1	0.292 (1)	−0.080 (1)	0.206 (1)	246 (20)	314 (21)	150 (12)	49 (17)	40 (12)	33 (13)	10.176
O2	0.008 (1)	0.265 (1)	−0.184 (1)	348 (25)	254 (19)	160 (12)	−1 (18)	7 (14)	+55 (12)	10.914
O3	0.381 (1)	0.299 (1)	0.078 (1)	293 (25)	308 (24)	191 (15)	−91 (19)	36 (15)	−20 (14)	11.576
O4	0.401 (1)	0.004 (1)	−0.115 (1)	189 (19)	355 (23)	185 (13)	12 (17)	79 (13)	1 (14)	10.676

[a] Standard deviations in parentheses refer to last digit quoted. [b] Anisotropic thermal parameters × 10^4 defined by $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. [c] Equivalent isotropic thermal parameter.

sample that had been kindly supplied by Dr. W. A. G. Graham and Mr. J. K. Hoyano. Preliminary photography (Cu Kα Weissenberg $hk0$, $hk1$, $hk2$, Mo Kα precession $h0l$) showed the crystals to be monoclinic, and the systematic absences ($h0l$, for $h + l = 2n + 1$, $0k0$ for $k = 2n + 1$) suggested the nonstandard space group $P2_1/n$. The nonstandard cell was retained over the standard $P2_1/n$ cell for the convenience of the β angle. Precise lattice parameters at 22° and their estimated standard deviations were obtained as $a = 9.212$ (1), $b = 10.131$ (1), $c = 12.749$ (1) Å, $\beta = 99.07$ (1)° from a least-squares fit of 2θ values that had been accurately centered on a Picker four-circle diffractometer using Cu Kα X-radiation (λ 1.54051 Å). The density, observed by flotation in aqueous zinc iodide as 2.04 (3) g cm^{-3}, is in poor agreement with that calculated for two molecules in the unit cell, 2.165 g cm^{-3}. We have no firm explanation for this poor agreement. The crystals had no defects that were visible by examination under the microscope. Contamination by the molybdenum analog was eliminated by mass spectrometry. A tentative explanation is that a small percentage of the sites in the crystal are occupied by solvent molecules rather than by the tungsten complex. For example, a 5% occupancy of n-hexane would produce the desired effect on the X-ray molecular weight, and would in fact improve the agreement between the observed and calculated elemental analysis figures for carbon, hydrogen, and silicon. The mass spectrum of a sample shows a strong peak at 86 amu which is, unfortunately, consistent with both $C_6H_{14}^+$ and the $Si(C_2H_5)_2^+$ fragments. However, the dimethylsilicon analog also shows an intense peak at 86 amu and in this case the only obvious source of the peak is the solvent, n-hexane.

Intensity data were collected on a Picker manual four-circle diffractometer using Cu Kα radiation, a graphite crystal monochromator (reflecting plane 002), and a takeoff angle of 2°. Reflections in range $0 < \theta < 50°$ were collected using a coupled $\omega/2\theta$ scan from $2\theta - 1°$ to $2\theta + 1°$ at a scan speed of 2°/min. Backgrounds were estimated by linear interpolation of 30-sec stationary crystal–stationary counter measurements at the limits of the scan. The crystal, of approximate dimensions 0.15 × 0.10 × 0.12 mm, was bounded by the faces of the forms {100} and {011} and was mounted with a^* coincident with the ϕ axis of the diffractometer. Eight well-distributed standard reflections were monitored periodically during the course of data collection and showed the decomposition to be dependent on time and $\sin\theta/\lambda$. An isotropic decomposition correction that was linear in both time and $\sin\theta/\lambda$ was found to give acceptable consistency (±2%) for the standard reflections. The $h00$ reflections ($h = 2, 4, 6$) were measured under varying conditions of ϕ ($0 \leq \phi \leq 180°$ in 5° intervals) to provide an assessment of the accuracy of the absorption correction. Of the 1214 reflections scanned, 945 were found to be above background using the criterion $I/\sigma(I) \geq 2.0$. The nine strongest intensities were reinvestigated for coincidence losses, and for none of these did the maximum count rate exceed the linear response range of the counter. The significant data were reduced to structure factor amplitudes by correction for Lorentz, polarization, decomposition, and absorption effects. Standard deviations $\sigma(F)$ for each observation were computed as described elsewhere using a p factor of 0.03.[5] The ϕ scan data after correction for absorption showed a remarkable consistency (better than ±1% on $|F|$ when counting statistics were negligible). The major programs used in this analysis, excluding local data reduction programs, were W. C. Hamilton's absorption program GONO9, C. T. Prewitt's SFLS5, A. Zalkin's Fourier program FORDAP, the Busing–Levy ORFFE program, and C. K. Johnson's ORTEP.

Solution and Refinement of the Structure

In the absence of disorder, the space group and unit cell contents impose symmetry 1 on the molecule and eliminate structures I, II, and III. Solutions for the approximate coordinates of tungsten and silicon atoms were readily obtained from a three-dimensional Patterson map, and the remaining nonhydrogen atoms were located from electron density difference maps. Structure factors were computed using the scattering factors of the neutral atoms[6] and included the real and imaginary components of anomalous scattering[7] for tungsten and silicon. The function minimized was $\Sigma w(|F_o| - |F_c|)^2$, with the unweighted and weighted residuals (R_1 and R_2, respectively) defined by

$$R_1 = \frac{\sum||F_o| - |F_c||}{\sum|F_o|} \qquad R_2 = \left(\frac{\sum w(|F_o| - |F_c|)^2}{\sum w|F_o|^2}\right)^{1/2}$$

where $w = 1/\sigma^2(|F_o|)$.

The refinement progress may be briefly outlined as follows.

Model	R_1	R_2
All atoms isotropic	0.11	0.11
W and Si anisotropic C and O isotropic	0.045	0.059
All atoms anisotropic	0.038	0.051

The final model with all atoms anisotropic may be justified from difference Fourier maps and the Hamilton test.[8] However, the isotropic decomposition correction model probably introduces a systematic error in the data, and anisotropic tensor elements are suspect. The introduction of the anisotropic thermal parameters did not change the fractional coordinates significantly. The anisotropic temperature factors are however necessary for attempting corrections for thermal motion.[9] The standard deviation of an observation of unit weight was 1.27 at the termination of the refinement when the largest shift was less than one-third of an estimated standard deviation in any parameter. Final

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(5) R. J. Doedens and J. A. Ibers, *Inorg. Chem.*, **6**, 204 (1967).

(6) D. T. Cramer and J. T. Waber, *Acta Crystallogr.*, **18**, 104 (1965).

(7) D. T. Cramer, *ibid.*, **18**, 17 (1965).

(8) W. C. Hamilton, *ibid.*, **18**, 502 (1965).

(9) W. R. Busing and H. A. Levy, *ibid.*, **17**, 142 (1964).

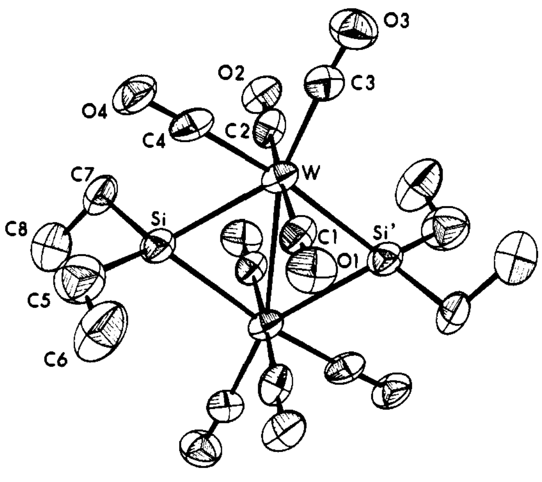

Figure 1. Perspective view of $W_2(CO)_8H_2\{Si(C_2H_5)_2\}_2$

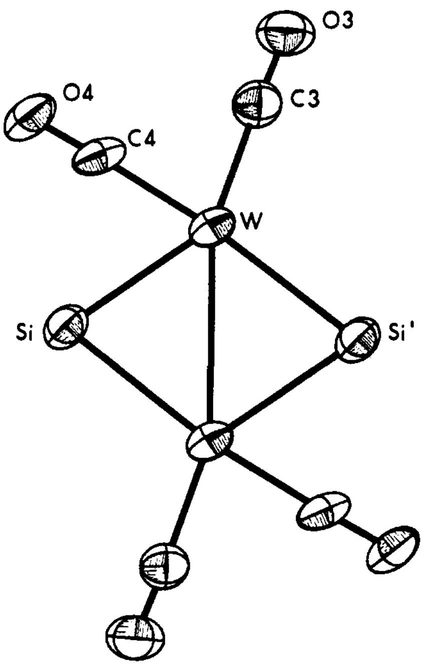

Figure 2. W_2Si_2 structural fragment.

electron density difference maps were computed using (i) all data and (ii) data with $\sin \theta/\lambda \leq 0.3$. No direct evidence for hydrogen atom locations was found, nor was any expected. The difference map, computed using all data, showed residual features in the range -0.41 to $+0.68$ e/Å^3. A table of the final observed and calculated structure factor amplitudes is available.[10] The final coordinate and thermal parameters are listed in Table I.

Discussion

The crystals contain discrete molecules, with no abnormal contacts for a molecular crystal, and therefore no intermolecular contacts are listed. The thermal parameters of all atoms are larger than normal in this type of crystal, and this would be compatible with a crystal containing vacancies or a fraction of the sites occupied by smaller molecules.

A perspective view of the molecule is shown in Figure 1. Because of the uncertainty in the location of the hydrogen atoms, a simple description of the tungsten coordination is not immediately worthwhile. The central cluster W_2Si_2 is planar within experimental error and the carbonyl groups C3O3, C4O4, C3′O3, and C4′O4′ (primed atoms related by $\bar{1}$) lie approximately in this plane. This structural fragment is shown in Figure 2. The remaining carbonyls are approximately perpendicular to this plane. A selection of intramolecular distances, angles, and planes are collected in Tables II, III, and IV, respectively.

The two tungsten atoms are separated by 3.18 Å, a distance that is consistent with a metal-metal bond. The metal-metal bond is further substantiated by the acute bridging angle of 74° found at the silicon atom.[11] The interesting and most important feature of this structural determination is the finding of two distinctly different tungsten-silicon distances, 2.586 (6) and 2.703 (4) Å. This highly significant difference we choose to interpret as evidence for direct insertion of a hydrogen atom into the longer tungsten-silicon bond. This is to be contrasted with the rhenium structures, where no differences have yet been detected.[2-4] The actual difference of 0.12 Å is not as large as that expected from a comparison of linear M–H–M and M–M systems, where a difference of 0.4 Å can be estimated.[12,13] An effect of the observed magnitude for the difference would be consistent with a nonlinear W–H–Si arrangement and is similar to the effect observed for the proposed bent Re–H–Re two-electron system in $Re_3H_2(CO)_{12}^-$.[14] Additional evidence for the nonlinearity of this group can be seen in the angular distribution of

Table II. Intramolecular Distances[a]

Atoms	Distance, Å Uncorr	Corr[b]	Corr[c]
W–W′ [d]	3.183 (1)		
W–Si	2.586 (5)	2.595 (5)	2.654 (5)
W–Si′	2.703 (4)	2.712 (4)	2.785 (5)
W–C1	1.94 (2)	1.95 (2)	2.04 (2)
W–C2	2.01 (2)	2.02 (2)	2.11 (2)
W–C3	1.98 (2)	2.00 (2)	2.09 (2)
W–C4	1.99 (2)	2.00 (2)	2.10 (2)
Si–C5	1.90 (3)	1.95 (3)	2.07 (2)
Si–C7	1.89 (2)	1.93 (2)	2.03 (2)
C1–O1	1.19 (2)	1.22 (2)	1.40 (1)
C2–O2	1.16 (2)	1.22 (2)	1.38 (1)
C3–O3	1.11 (2)	1.16 (2)	1.37 (1)
C4–O4	1.13 (2)	1.17 (2)	1.39 (1)
C5–C6	1.25 (3)	1.30 (3)	1.60 (2)
C7–C8	1.55 (2)	1.56 (3)	1.78 (2)

[a] Standard deviations in parentheses refer to last digit quoted. [b] Correction for thermal motion; second atom assumed to ride on first atom. [c] Correction for thermal motion; atoms assumed to move independently. [d] Primed atoms related by an inversion center.

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(10) A table of observed and calculated structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Reprint Department, ACS Publications, 1155 Sixteenth St., N.W., Washington, D. C. 20036, by referring to author, title of article, volume, and page number. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche.

(11) L. F. Dahl, E. R. deGil, and R. D. Feltham, *J. Amer. Chem. Soc.*, **91**, 1653 (1969), and references therein.

(12) L. B. Handy, P. M. Treichel, and L. F. Dahl, *ibid.*, **88**, 366 (1966).

(13) H. D. Kaesz, R. Bau, and M. R. Churchill, *ibid.*, **89**, 2775 (1967).

(14) M. R. Churchill, P. H. Bird, H. D. Kaesz, R. Bau, and B. Fontal, *ibid.*, **90**, 7135 (1968).

Table III. Intramolecular Angles[a]

Atoms	Angle, deg	Atoms	Angle, deg
W′-W-Si[b]	54.70 (10)	C2-W-C4	90.2 (6)
W′-W-Si′	51.33 (10)	C3-W-C4	78.4 (7)
Si-W-Si′	106.03 (12)	W-Si-W′	73.97 (12)
Si-W-C1	88.9 (5)	W-Si-C5	123.8 (9)
Si-W-C2	93.0 (4)	W-Si-C7	114.3 (6)
Si-W-C3	144.8 (5)	C5-Si-C7	101.0 (11)
Si-W-C4	66.6 (5)	W-C1-O1	173.6 (14)
Si′-W-C3	109.1 (5)	W-C2-O2	177.1 (14)
C1-W-C2	177.1 (6)	W-C3-O3	178.8 (17)
C1-W-C3	89.0 (7)	W-C4-O4	177.3 (16)
C1-W-C4	92.5 (7)	Si-C5-C6	115.1 (24)
C2-W-C3	90.6 (7)	Si-C7-C8	112.2 (14)

[a] Standard deviations in parentheses refer to last digit quoted. [b] Primed atoms related by an inversion center.

Table IV. Selected Least-Squares Planes

Atoms defining plane[a]		Equation of plane[b,c]	Deviations			
W	Si	$+0.262X - 0.526Y + 0.809Z = 0$	W	0.0000	Si	+0.0001
			C3	+0.091	O3	+0.064
			C4	−0.099	O4	−0.166
W	Si	$+0.269X - 0.536Y + 0.800Z = 0$	W	+0.0002	Si	+0.033
C3	O3		C3	+0.081	O3	+0.048
C4	O4		C4	−0.073	O4	−0.124
W		$-0.450X + 0.640Y + 0.0623Z = 0$	W	+0.0006		
C1	O1		C1	+0.065	O1	+0.070
C2	O2		C2	+0.035	O2	+0.079

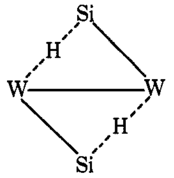
[a] And equivalent atoms related by $\bar{1}$. [b] Referred to the Cartesian coordinate system with the *X*, *Y*, and *Z* axes defined by the directions of *a*, *b*, and *c**, respectively. [c] Computed using MGEOM, a molecular geometry program by J. S. Wood.

ligands as shown by Figure 2. An estimate of the length of a silicon–tungsten σ bond is difficult in this type of molecule. A covalent radius of 1.17 Å for silicon[15a] appears to be suitable, but the value for the tungsten radius can be estimated as either 1.30[15b] or 1.62 Å[16] (making the assumption that the covalent radii of tungsten and molybdenum would be virtually identical). The predicted values for a tungsten–silicon bond are then 2.47 and 2.79 Å. Both of the silicon–tungsten distances observed in this structure are within these limits. It may be argued that the calculated value of 2.78 Å would be more appropriate for this type of molecule, and a discussion of shortening would then be in order. It is possible to invoke direct silicon–tungsten π bonding, and a concomitant increase in tungsten–silicon bond order, over both the shorter and longer tungsten–silicon distances, on purely geometric grounds. The observation of bond shortening does not prove the existence of extensive π bonding, since it can be interpreted by changes in the σ bonding from the arbitrary standard on which the covalent radius is based. However, Graham's semiquantitative treatment of infrared data suggests that σ bonding is an important feature of transition metal–silicon bonding.[17]

The average tungsten–carbon (carbonyl) distance is 1.98 Å (uncorrected), and the average carbon–oxygen distance is 1.15 Å (also uncorrected). These distances are not determined with sufficient precision to warrant comparison with one another within the framework of differences in their chemical environment. The value for W-C(O) does agree with those (average 1.96) observed in other tungsten carbonyl derivatives whose structures are known.[18–21]

The geometry of the diethylsilicon group shows no unusual features. The two independent silicon–carbon distances show good internal agreement, and the average (assuming the model for thermal motion correction) is 1.94 Å, the value that would be predicted on the basis of covalent radii.[15] The carbon–carbon distances of the two ethyl groups show a significant difference unless the independent motion model is applied to the ethyl group C5C6 while the uncorrected or riding model is used for C7C8.

The high thermal parameters of this structure have made consideration of the relative thermal motion of the atoms necessary, and a strong personal bias has been used to select the appropriate model in one instance. However, the main feature of this molecule is the central W_2Si_2 unit which should be a relatively rigid group. The motions of such a rigid group could not product tungsten–silicon distances as different as the values observed in this structure. The bonding of the central unit may be described in simple bonding fragments as



i.e., a metal–metal bond, two W—Si σ bonds, and two bent three-center two-electron W···H—Si bonds (the two electrons being supplied by the silicon and hydrogen atoms). This simple view is useful in that it provides a simple formalism for electron counting in the application of the inert gas electron configuration. It is this description of the bonding that allows the tungsten coordinates to be discussed in terms of a pentagonal bipyramid. The two axial bonds are then to the carbonyl groups C1O1 and C2O2, and the five equatorial sites correspond to the two remaining carbonyls, the tungsten–silicon bond, the tungsten–tungsten bond, and the three-center two-electron W-H-Si bond. However, a molecular orbital description may be preferable, and a treatment of this and related complex bridging systems is currently under consideration.[22]

The definite insertion of the hydrogen atom into the tungsten–silicon bond rather than **1** may well be a property of this particular arrangement where each silicon or tungsten atom has only one hydrogen as a close neighbor, or may be the result of steric crowding. We believe that this is the only true hydrogen-bridged silicon–transition metal bond that has been investigated in this series and that the molecules $Re_2(CO)_8H_2Si(C_6H_5)_2$, $Re_2(CO_6H_4(Si(C_2H_5)_2)_2$, and $Re_2(CO)_7H_2$-

(15) L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1960: (a) p 246; (b) p 256.

(16) M. J. Bennett and R. Mason, *Nature (London)*, **205**, 760 (1965).

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$(Si(C_2H_5)_2)_2$ (ref 3, 4, and 23, respectively) all contain simple terminal hydrogens. The plausibility of the weak bridge system (II and V) remained as a result of our initial studies of another series of silyl derivatives, *viz.*, $LMHSiR_3$. These studies now include the complete structural determination of the compounds $(h^5\text{-}C_5H_5)Mn(CO)_2HSi(C_6H_5)_3$, $(h^5\text{-}C_5H_5)Mn(CO)_2HSiCl_2C_6H_5$, $Fe(CO)_4HSi(C_6H_5)_3$, and $(h^5\text{-}C_5H_5)Re(CO)_2HSi(C_6H_5)_3$ (ref 24, 25, 26, and 27, respectively). The weak silicon–hydrogen bridge[24,25] appears to result from the particularly crowded environment of the manganese atoms in the first two structures and does not appear in the iron or rhenium compounds. Previous speculation[1,3] on the use of the infrared silence of the metal–hydrogen stretch in these systems would appear to be doubtful. Our current view is that the bridges arise only in sterically crowded situations, and the dinuclear rhenium species do not qualify in this respect. This point will be discussed in detail in future papers in this series.

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Kinetic and Equilibrium Studies on Azidochromium(III) Ion in Concentrated Perchloric Acid[1]

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Abstract: The spectrum of azidochromium(III) ion in perchloric acid shows a dependence upon acidity which is consistent with protonation; the derived acid dissociation constant $K_1 = [CrN_3^{2+}]h_0/[CrN_3H^{3+}]$ is equal to 2.7×10^3 at 30°. The rate of aquation of azidochromium(III) ion in concentrated perchloric acid (1–11 *M*) at 30° is correlated with the solution composition by the rate law $-\mathrm{d}\ \ln\ [CrN_3]_T/\mathrm{d}t = (k_2a_w + k_3)h_0/(K_1 + h_0)$, with $k_2 = 2.7 \times 10^{-3}\ \text{sec}^{-1}$, $k_3 = 1.8 \times 10^{-4}\ \text{sec}^{-1}$, and $K_1 = 2.70 \times 10^3$ (the value determined from spectra). This rate law indicates that aquation occurs by both SN2 and SN1 pathways. The Henry's law constant for hydrazoic acid was evaluated for perchloric acid solutions with a range of concentrations (0.1–11 *M*); in solutions of high acidity (>8 *M*), hydrazoic acid is protonated, thereby lowering the Henry's law constant.

The aquation reactions of coordination complexes containing relatively basic ligands are governed by rate laws with terms involving a positive dependence upon the concentration of hydrogen ion in addition to the generally observed inverse dependences. Swaddle and King[2] found that the rate law

$$-\frac{\mathrm{d}\ \ln\ [CrN_3^{2+}]}{\mathrm{d}t} = k_1[H^+] + k_0 + k_{-1}[H^+]^{-1} + k_{-2}[H^+]^{-2}$$

correlates the rate of aquation of pentaaquoazidochromium(III) ion[3]

$$Cr(OH_2)_5N_3^{2+} + H_3O^+ = Cr(OH_2)_6^{3+} + HN_3$$

over the range of hydrogen ion concentration 10^{-3}–1 *M*. The present paper deals with studies at 30° which extend the acidity range to 11 *M* perchloric acid.

The purpose of extending the acidity range was to determine, if possible, the basicity of azidochromium(III) ion[4,5] and to investigate the appropriateness of using the Hammett acidity function in correlating the basicity of a basic coordination complex of charge 2+. In this study both spectrophotometric and kinetic data have been employed to seek these objectives. The protonation of hydrazoic acid in concentrated perchloric acid also has been studied at 30° by evaluation of the Henry's law constant for hydrogen azide in such solutions.

Experimental Methods

Equipment and Reagents. Spectrophotometric measurements were made with a Cary Model 15 spectrophotometer. In the study

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(1) Taken in part from the Ph.D. Thesis of J. C. T., University of Colorado, 1970. This work was supported by National Science Foundation Grant No. GP7185-X.

(2) T. W. Swaddle and E. L. King, *Inorg. Chem.*, **3**, 234 (1964).

(3) In general, the complete coordination shell will not be specified; this species will be called simply azidochromium(III) ion.

(4) Appreciable protonation of other azide complexes has been observed.[5]

(5) (a) $Co(CN)_5N_3^{3-}$: A. Haim and W. K. Wilmarth, *Inorg. Chem.*, **1**, 583 (1962); (b) *trans*-$Co(en)_2Cl(N_3)^+$: P. J. Staples, *J. Chem. Soc.*, 7320 (1965); (c) $Cr(NH_3)_5N_3^{2+}$, $Co(NH_3)_5N_3^{2+}$, and $Rh(NH_3)_5N_3^{2+}$: *ibid.*, *A*, 2731 (1968); (d) $Rh(NH_3)_5N_3^{2+}$: C. S. Davis and G. C. Lalor, *ibid.*, *A*, 445 (1970).