appreciably when the correlation among the data is ignored.

$$\chi^2 = \mathbf{H}'\mathbf{M}^{-1}\mathbf{H} = \Sigma h'_i m_i^{-1} h_i \qquad (i = 1, J) \qquad (22)$$

In fact, it appears that the only error that is made upon ignoring the correlation among experimental errors is that one would always conclude, upon examining the matrix of partial correlation coefficients, that the molar absorptivities of the same species at different wavelengths are linearily uncorrelated whereas in reality this is only true if $s^2(A) > \alpha^2 s^2(C_M)$. One obtains accurate values for the linear correlation among the other parameters whether or not one considers the correlation among the errors in the data.

It is fortunate that significant correlation of the equilibrium constants with each other and with the molar absorptivities does not adversely affect the iteration to the minimum because the degree of correlation between parameters cannot be altered dramatically by simple changes in the experimental procedure. For example, a uniform change in the precision of the data does not change the correlation between parameters since a partial correlation coefficient is the *ratio* of elements in the $\mathbf{A}'\mathbf{M}^{-1}\mathbf{A}$ matrix. An increase in the number of wavelengths at which measurements are made is also ineffective for reducing the correlation between parameters although this does decrease the estimated error in the formation constants by increasing the number of degrees of freedom in the system. The only effective way to reduce the correlation between parameters appears to be to include in the calculation data for solutions of known composition.

From a purely practical point of view, it should be noted that it is considerably simpler to write computer programs based on the matrix formulation than on the normal equations implicit in eq 15–18. If the matrix formulation is used, it is a trivial matter to include the correlation of experimental errors, and therefore we recommend that this be done even though ignoring this correlation will probably not change the results significantly.

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The Crystal Structure of Di-μ-hydrido-diphenylsiliconbis(tetracarbonylrhenium), $(C_6H_5)_2SiH_2Re_2(CO)_8$

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The crystal structure of di-μ-hydrido-diphenylsiliconbis(tetracarbonylrhenium), $(C_6H_5)_2SiH_2Re_2(CO)_8$, has been determined from three-dimensional X-ray data collected by counter methods. Refinement by least-squares techniques gave a final R factor of 5.6% for 1297 independent above-background reflections. The space group is orthorhombic, D_{2h}^{14}-Pbcn, with cell parameters a = 17.657 (7) Å, b = 17.294 (7) Å, and c = 15.426 (5) Å. The calculated density of 2.20 (1) g cm^{-3} (26°) for eight molecules per unit cell agrees with the value of 2.23 (2) g cm^{-3} measured by flotation. The molecule exhibits an Re–Re bond of 3.121 (2) Å which is bridged symmetrically by the silicon atom with Re–Si distances of 2.544 (9) Å. The carbonyl groups occupy octahedral positions about the rhenium atoms while the two ligand hydrogen atoms are assumed to occupy the vacant octahedral coordination site of each rhenium atom, bridging the Re–Si bonds and lying in the ReReSi plane. The molecular symmetry approximates closely to C_{2v}.

Introduction

The ultraviolet irradiation of a solution of $Re_2(CO)_{10}$ and $(C_6H_5)_2SiH_2$ in benzene yields the compound $(C_6H_5)_2SiH_2Re_2(CO)_8$.[2] The mass spectrum indicates that there are 12 hydrogen atoms in the molecule and the proton nmr and the infrared spectra are consistent with the presence of two hydrogen atoms, bridging the Re–Si bonds. Hydrogen bridges are known in rhenium and manganese carbonyls such as $HRe_2Mn(CO)_{14}$[3a] and $H_2Re_3(CO)_{12}^-$,[3b] and there are a number of compounds with hydrogen bridges involving boron and a transition metal, such as $HMn_3(CO)_{10}(BH_3)_2$,[4] $[(C_6H_5)_3P]_2CuBH_4$,[5] and $[(CH_3)_4N][Cr(CO)_4B_3H_8]$,[6] but this is the first such mixed bridge where a nontransition element other than boron is involved. With the availability of good crystals the crystal structure analysis was undertaken in order to provide stereochemical evidence as to the structure of this new compound.

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(1) Department of Chemistry, The University, Sheffield, S3 7HF, England.

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Experimental Section

Crystals of di-μ-hydrido-diphenylsiliconbis(tetracarbonylrhenium), $Re_2(CO)_8H_2Si(C_6H_5)_2$, were kindly supplied by Professor W. A. G. Graham and Mr. J. M. Hoyano. Preliminary investigation of the colorless crystals showed mmm diffraction symmetry. Cell parameters were obtained from the Mo Kα precession photographs of the levels ($hk0$) and ($h0l$). They were a = 17.657 (7) Å, b = 17.294 (7) Å, and c = 15.426 (5) Å (λ 0.71069 Å, 26°). The method of film calibration and the calculation of these parameters and their errors have been described previously.[7] The orthorhombic space group D_{2h}^{14}-Pbcn was the only one consistent with the Laue symmetry and the systematic absences observed on the precession photographs and on Weissenberg photographs of levels ($0kl$)-($3kl$) taken with Cu Kα radiation. These absences were: ($0kl$), $k = 2n + 1$; ($h0l$), $l = 2n + 1$; ($hk0$), $h + k = 2n + 1$. An experimental density of 2.23 (2) g cm^{-3} was obtained by flotation in a mixture of dibromoethane and dibromomethane. The density calculated for eight molecules per unit cell is 2.20 (1) g cm^{-3} which implies that all atoms are in general positions so that no symmetry need be imposed on the molecule.

The crystal used for data collection was a sphere of radius 0.17 mm (±6%) which was ground in a compressed-air abrasion chamber such as is described by Bond.[8] It was mounted in a thin-walled glass capillary to minimize the decomposition indicated by the rapid discoloration of crystals photographed exposed to the atmosphere. Intensity data were collected on a Pailred fully automated diffractometer equipped with a scintillation counter. Mo Kα radiation was used, monochromatized from graphite, with a takeoff angle of 6.0°. The counter aperture was 2.5°. An ω-scan procedure was used with a scan range of 1.2° for the zero layer, increasing to 2.0° with greater peak width toward the higher μ values of the upper levels. The scan speed was 2.5°/min and background was counted for 10 sec at the extremes of the scan range. Data were collected from levels ($0kl$) to ($16kl$) within the range $2\theta \leq 44°$, beyond which point there were very few reflections of measurable intensity. The crystal was then rotated by 180° about the ω axis and the data collection was repeated for the levels ($0k\bar{l}$)-($16k\bar{l}$). Thus the four equivalent forms (hkl), ($h\bar{k}l$), ($hk\bar{l}$), and ($h\bar{k}\bar{l}$) were measured giving a total of 8700 reflections. Eight reflections from well-spaced regions of the zero level were measured after each layer had been collected as a check on electronic and crystal stability. A small increase in intensity was observed, amounting to 10% of starting intensity by the time 20 levels had been collected. From this point the intensities of the standard reflections showed only random fluctuations of no more than 2% intensity. The increase was independent of θ and was attributed to surface changes on the graphite monochromator which was being used for the first time. There were no indications of electronic instability and no evidence in both earlier and later data collections with the instrument that such instability was causing the variation. By the end of the data collection, during which the crystal was continuously exposed for 17 days, the crystal showed a slight brown discoloration. Thus it is possible that crystal decomposition accounted for the leveling out of the intensity increase. The increase is not attributed to increasing crystal mosaicity in the initial stages of decomposition. The shock of crystal grinding should already have increased mosaicity and the crystal had previously been exposed to X-rays for 3 days during preliminary photography. Since the intensity increase of the standard reflections was small and regular, a single corrective scale factor was applied to the data of each level, from a plot of the mean normalized standard reflection intensities against time. The intensity variances were calculated from $\sigma^2(I) = T + t^2B + (pI)^2$ where $p = 0.06$, T is the total scan count, B is the total background count, t is the scale factor that brings B and T to the same time scale, and I is the corrected intensity, $T - tB$. Lorentz and polarization corrections were applied to all data together with a correction for absorption. The linear absorption coefficient for the radiation used was 118 cm^{-1} and the transmission factors were in the range 0.061-0.073. The data were then combined by computing the weighted means and equivalent standard deviations of the corrected intensities for each group of (usually) four equivalent reflections according to the formulas: $I_{\text{mean}} = \Sigma_i w_i I_i / \Sigma w_i$ and $\sigma(I_{\text{mean}}) = (1/\Sigma w_i)^{1/2}$, where $w_i = 1/\sigma^2(I_i)$. A total of 2265 independent observations resulted, of which 968 were rejected as below background using the criterion $\sigma(I_{\text{mean}}) \geq 0.4 I_{\text{mean}}$ for rejection.

Structure Solution and Refinement

The Re atoms were located by inspection of the three-dimensional Patterson function, sharpened to point atoms at rest.[9] The remaining nonhydrogen atoms were located by Fourier syntheses and the structure was refined by full-matrix least-squares methods. The function minimized was $\Sigma w(|F_o| - |F_c|)^2$ where $w = 1/\sigma^2(F)$ was derived from the previously defined $\sigma^2(I)$. The agreement factors were defined by $R_1 = \Sigma(||F_o| - |F_c||)/\Sigma|F_o|$ and $R_2 = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$. The scattering factors for neutral rhenium, silicon, oxygen, and carbon were by Cromer,[10] with correction for anomalous dispersion included in the structure factor calculation for Re ($\Delta f' = -1.34$, $\Delta f'' = 7.34$) and Si ($\Delta f' = 0.09$, $\Delta f'' = 0.09$).[11] The hydrogen curve was that determined experimentally by Mason and Robertson.[12] The carbon atoms of the two phenyl groups were refined as rigid bodies having D_{6h} symmetry, C-C = 1.397 Å. The phenyl hydrogen atoms were included in their calculated positions (C-H = 1.08 Å) and given the temperature factors of the carbon atoms to which they were attached. Their positional and thermal parameters were not refined but reset after each cycle. The agreement factors were $R_1 = 0.077$ and $R_2 = 0.079$ after four cycles with all atoms except the two hydride atoms included with individual anisotropic temperature factors. When the Re and Si atoms were given anisotropic thermal parameters on the evidence of a difference electron density map, the agreement factors were reduced significantly to $R_1 = 0.056$ and $R_2 = 0.057$ after two cycles. A barely significant[13] R-factor decrease occurred when the remaining nongroup atoms were refined with anisotropic thermal parameters, but the resulting thermal ellipsoids were physically unreasonable and refinement in this way was unjustifiable. In a final structure factor calculation the unobserved data were included. There were no unobserved reflections for which the calculated values were greater than the threshold values by more than 2σ. The final difference electron density map revealed no anomalous regions of electron density.

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[7] M. Elder, *Inorg. Chem.*, **8**, 2703 (1969).

[8] W. L. Bond, *Rev. Sci. Instr.*, **22**, 344 (1951).

[9] All computing was carried out on an IBM 360/67 computer. The crystallographic program system of F. R. Ahmed, Ottawa, was used, together with a number of local programs. Least-squares refinement was carried out with C. T. Prewitt's SLFS5, modified for group refinement by M. J. Bennett and B. Foxman. The molecular geometry program ORFFE2, by W. R. Busing and H. A. Levy, modified by R. J. Doedens was also used together with C. K. Johnson's plotter program, ORTEP.

[10] D. T. Cromer, *Acta Cryst.*, **A24**, 321 (1968).

[11] D. T. Cromer, *ibid.*, **18**, 20 (1965).

[12] R. Mason and G. B. Robertson in "Advances in Structure Research by Diffraction Methods," Vol. 2, R. Brill and R. Mason, Ed., Interscience Division, John Wiley and Sons, Inc., New York, N. Y., 1966, p 57.

[13] W. C. Hamilton, "Statistics in Physical Science," The Ronald Press Co., New York, N. Y., 1964, p 157.

Table I

Observed and Calculated Structure Factor Amplitudes in Electrons (×10)

The residual density was everywhere less than 1.0 $e^-/\text{Å}^3$, on which scale a carbon atom in the final $|F_o|$ Fourier map was about 4.5 $e^-/\text{Å}^3$, and the highest regions were very close to the Re atom positions. The two hydride ligands could not be located. The weighting scheme used in refinement appears to be valid in view of the standard deviation of an observation of unit weight, 1.07, which is close to the theoretical value of 1.00. The criterion that the average value of $w(|F_o| - |F_c|)^2$ should be constant for all classes of reflections was met according to the evidence of plots of this function against $(\sin^2 \theta)/\lambda^2$ and against $|F_o|$. There was no indication of the necessity for a correction for secondary extinction. The final values of $|F_o|$ and $|F_c|$ are listed in electrons (×10) in Table I. The final atomic parameters are listed in Table II together with their standard deviations obtained from the last refinement cycle, in which all parameters were varied.

The parameters for the phenyl groups are listed in Table III together with the derived positional parameters for the carbon atoms. The angles *D*, *E*, and *F* and the axial system used for the group refinement are defined in a paper by Beauchamp, *et al.*[14] The atoms of the phenyl groups have two numbers. C(*ji*) is carbon atom *i* of ring *j*, where $i = 1$ refers to an atom bonded to silicon and the numbers continue in cyclic order around each ring. The hydrogen atoms have the numbers of the carbon atoms to which they are bonded.

Results

The molecular structure of $(C_6H_5)_2SiH_2Re_2(CO)_8$ is shown viewed down the *y* axis in the stereopair of

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(14) A. L. Beauchamp, M. J. Bennett, and F. A. Cotton, *J. Am. Chem. Soc.*, **90**, 6675 (1968).

TABLE II

FINAL POSITIONAL AND THERMAL ATOMIC PARAMETERS

Atom	x/a	y/b	z/c	B, Å^2
Re(1)	0.22903 (7)[a]	0.19992 (8)	0.20131 (8)	4.4[b]
Re(2)	0.13799 (8)	0.05846 (8)	0.13110 (9)	4.6[b]
Si	0.2026 (5)	0.1646 (5)	0.0441 (6)	4.4[b]
C(1)	0.3228 (16)	0.1389 (17)	0.2011 (20)	4.4 (6)
O(1)	0.3751 (13)	0.0990 (13)	0.1964 (16)	6.5 (5)
C(2)	0.1375 (18)	0.2599 (17)	0.1995 (21)	5.3 (7)
O(2)	0.0816 (13)	0.2964 (13)	0.2017 (16)	7.3 (5)
C(3)	0.2892 (24)	0.2846 (23)	0.2384 (27)	8.4 (11)
O(3)	0.3218 (16)	0.3419 (15)	0.2534 (18)	8.4 (7)
C(4)	0.2017 (20)	0.1625 (22)	0.3244 (27)	6.7 (9)
O(4)	0.1924 (17)	0.1386 (17)	0.3901 (21)	10.0 (8)
C(5)	0.2298 (18)	−0.0006 (19)	0.1277 (22)	5.2 (7)
O(5)	0.2857 (14)	−0.0423 (13)	0.1257 (17)	7.6 (6)
C(6)	0.0445 (20)	0.1223 (18)	0.1364 (23)	5.8 (8)
O(6)	−0.0085 (14)	0.1590 (14)	0.1384 (17)	7.4 (6)
C(7)	0.0877 (25)	−0.0217 (24)	0.0844 (27)	7.7 (11)
O(7)	0.0558 (19)	−0.0773 (17)	0.0503 (21)	10.8 (9)
C(8)	0.1128 (25)	0.0173 (24)	0.2547 (34)	8.8 (12)
O(8)	0.1061 (16)	0.0041 (16)	0.3250 (21)	8.9 (8)

Atom	β_{11}[c]	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Re(1)	0.00388 (4)	0.00431 (6)	0.00354 (6)	−0.00020 (6)	−0.00054 (5)	−0.00073 (6)
Re(2)	0.00397 (5)	0.00376 (6)	0.00467 (7)	−0.00058 (5)	0.00015 (6)	−0.00014 (7)
Si	0.0035 (3)	0.0043 (4)	0.0039 (5)	−0.0008 (3)	−0.0008 (3)	−0.0005 (4)

[a] In this and following tables, values in parentheses are the standard deviations in the last significant figures. [b] An equivalent isotropic temperature factor computed from $B_{eq} = {}^4/_3(\beta_{11}a^2 + \beta_{22}b^2 + \beta_{33}c^2 - 2\beta_{12}ab - 2\beta_{13}ac - 2\beta_{23}ab)$. [c] The anisotropic ellipsoid has the form: $\exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})]$.

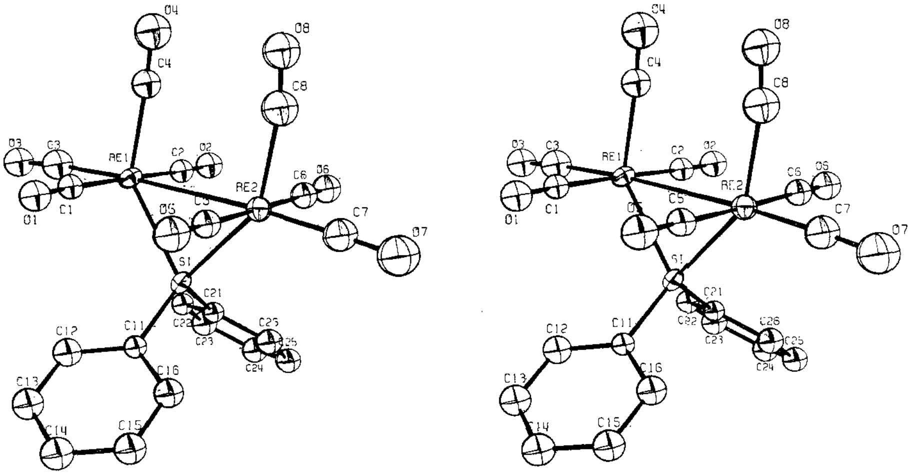

Figure 1.—Stereoscopic drawing of a molecule of $(C_6H_5)_2SiH_2Re_2(CO)_8$. Thermal ellipsoids are scaled to include 20% probability. The two hydrogen atoms are presumed to bridge the Re–Si bonds, lying in the plane of the ReReSi triangle.

TABLE III

RIGID-BODY PARAMETERS

A. Ring Origins and Rotation Angles

	Origin coordinates			Angles, radians		
Ring	x	y	z	D	E	F
1	0.3457 (8)	0.1139 (8)	−0.0769 (10)	3.804 (13)	0.397 (17)	3.500 (16)
2	0.0926 (8)	0.2830 (9)	−0.0638 (9)	3.120 (14)	2.424 (13)	2.462 (13)

B. Derived Positional Coordinates and Isotropic Temperature Factors

Atom	x	y	z	B, Å^2
C(11)	0.2839 (16)	0.1362 (13)	−0.0254 (14)	3.9 (6)
C(12)	0.3523 (15)	0.1769 (11)	−0.0196 (15)	6.4 (8)
C(13)	0.4140 (14)	0.1545 (12)	−0.0712 (12)	7.0 (9)
C(14)	0.4074 (16)	0.0913 (13)	−0.1285 (14)	7.5 (9)
C(15)	0.3391 (15)	0.0507 (11)	−0.1342 (15)	6.7 (9)
C(16)	0.2774 (14)	0.0731 (12)	−0.0827 (12)	6.1 (8)
C(21)	0.1396 (11)	0.2320 (12)	−0.0177 (12)	4.0 (6)
C(22)	0.1478 (11)	0.3122 (13)	−0.0068 (10)	5.0 (7)
C(23)	0.1007 (13)	0.3632 (9)	−0.0529 (15)	7.4 (9)
C(24)	0.0454 (11)	0.3341 (12)	−0.1099 (12)	7.5 (9)
C(25)	0.0373 (11)	0.2539 (13)	−0.1207 (10)	6.5 (9)
C(26)	0.0844 (13)	0.2029 (9)	−0.0747 (15)	6.2 (8)

Figure 1. The orientations of the thermal ellipsoids for the atoms that were refined anisotropically are indicated in this figure. The presumed positions of the ligand hydrogen atoms are not shown. The evidence for their existence based upon nmr, infrared, and mass spectral data has already been presented.[2] Since they were not located in this work, there can be no direct X-ray evidence for their presence. Indirect evidence arises from the fact that the inclusion in distance calculations of two hydrogen atoms at calculated sites (in the ReReSi plane with an Re–H bond of 1.68 Å at 90° to the Re–Re bond) leads to no intra- or intermolecular nonbonded contacts that are abnormally short. The molecular geometry is tabulated in Tables IV and V. A modified copy of ORFFE2, previously described,[7] was used for these calculations and cell parameter errors were taken into account in the stand-

TABLE IV

INTRAMOLECULAR DISTANCES, Å

Bonding		Nonbonding	
Re(1)–Re(2)	3.121 (2)	C(3)···C(1)	2.65 (5)
Re(1)–Si	2.544 (9)	C(3)···C(2)	2.78 (5)
Re(2)–Si	2.544 (9)	C(3)···C(4)	2.93 (6)
Re(1)–C(1)	1.96 (3)	C(1)···C(4)	2.89 (5)
Re(1)–C(2)	1.92 (3)	C(2)···C(4)	2.80 (5)
Re(1)–C(3)	1.90 (4)	C(7)···C(5)	2.62 (6)
Re(1)–C(4)	2.06 (4)	C(7)···C(6)	2.73 (5)
Re(2)–C(5)	1.92 (3)	C(7)···C(8)	2.82 (6)
Re(2)–C(6)	1.99 (4)	C(5)···C(8)	2.86 (6)
Re(2)–C(7)	1.80 (5)	C(6)···C(8)	2.84 (6)
Re(2)–C(8)	2.08 (5)	C(1)···C(5)	3.13 (4)
C(1)–O(1)	1.16 (3)	O(1)···O(5)	3.11 (3)
C(2)–O(2)	1.17 (4)	C(2)···C(6)	3.05 (4)
C(3)–O(3)	1.17 (4)	O(2)···O(6)	3.02 (3)
C(4)–O(4)	1.11 (4)	C(4)···C(8)	3.15 (6)
C(5)–O(5)	1.22 (3)	O(4)···O(8)	2.96 (4)
C(6)–O(6)	1.13 (3)	C(11)···C(21)	3.05 (2)
C(7)–O(7)	1.23 (4)		
C(8)–O(8)	1.11 (5)		
Si–C(11)	1.87 (2)		
Si–C(21)	1.88 (2)		

TABLE V

BOND ANGLES, DEG

Re(2)–Re(1)–Si	52.2 (2)	Re(1)–Re(2)–Si	52.2 (2)
Re(2)–Re(1)–C(1)	90.7 (8)	Re(1)–Re(2)–C(5)	89.5 (9)
Re(2)–Re(1)–C(2)	88.1 (9)	Re(1)–Re(4)–C(6)	88.7 (9)
Re(2)–Re(1)–C(3)	176.3 (12)	Re(1)–Re(2)–C(7)	176.6 (13)
Re(2)–Re(1)–C(4)	87.3 (10)	Re(1)–Re(2)–C(8)	93.4 (12)
Si–Re(1)–C(1)	91.4 (9)	Si–Re(2)–C(5)	89.5 (10)
Si–Re(1)–C(2)	87.8 (10)	Si–Re(2)–C(6)	89.6 (10)
Si–Re(1)–C(3)	125.1 (13)	Si–Re(2)–C(7)	124.5 (13)
Si–Re(1)–C(4)	139.4 (10)	Si–Re(2)–C(8)	145.6 (12)
C(1)–Re(1)–C(2)	179.0 (13)	C(5)–Re(2)–C(6)	178.2 (13)
C(1)–Re(1)–C(3)	86.8 (15)	C(5)–Re(2)–C(7)	89.8 (16)
C(1)–Re(1)–C(4)	91.8 (13)	C(5)–Re(2)–C(8)	91.3 (16)
C(2)–Re(1)–C(3)	93.4 (15)	C(6)–Re(2)–C(7)	92.0 (16)
C(2)–Re(1)–C(4)	89.2 (14)	C(6)–Re(2)–C(8)	88.5 (16)
C(3)–Re(1)–C(4)	95.5 (16)	C(7)–Re(2)–C(8)	89.9 (17)
Re(1)–Si–Re(2)	75.7 (3)	Re(2)–Si–C(11)	117.4 (8)
Re(1)–Si–C(11)	118.4 (7)	Re(2)–Si–C(21)	117.0 (7)
Re(1)–Si–C(21)	116.6 (7)	C(11)–Si–C(21)	108.8 (10)
Re(1)–C(1)–O(1)	174 (3)	Re(2)–C(5)–O(5)	176 (3)
Re(1)–C(2)–O(2)	177 (3)	Re(2)–C(6)–O(6)	179 (3)
Re(1)–C(3)–O(3)	172 (4)	Re(2)–C(7)–O(7)	177 (4)
Re(1)–C(4)–O(4)	174 (4)	Re(2)–C(8)–O(8)	170 (4)

TABLE VI

LEAST-SQUARES PLANES[a]

Atoms	A	B	C	D	χ^2	$\chi_{n-3,\,0.05}{}^2$
Re(1)–Re(2)–Si–C(3)–C(4)–C(7)–C(8)	0.8391	−0.5435	−0.0230	−1.4498	12.8	13.3
Deviations:[b] C(4) −0.10 (4), C(3) 0.08 (4)						
Re(1)–Re(2)–C(1)–C(2)–C(3)–C(5)–C(6)–C(7)	0.1754	0.2960	−0.9390	1.1464	15.6	15.1
Deviations:[b] C(3) 0.09 (4), C (7) 0.10 (4)						

[a] The plane equations are in ångström units and have the form $AX + BY + CZ + D = 0$ with respect to an orthogonal-axis system given by $X \equiv a$, $Y \equiv b$, $Z \equiv c$. [b] Deviations greater than 1.5σ are given. The interplanar angle is 89.7°.

ard errors. The intermolecular distances are normal. The only ones less than the sum of appropriate van der Waals radii are two O···H distances of 2.55 and 2.58 Å, respectively. The minimum O···O contact between molecules is 3.24 Å, H···H 2.65 Å. Least-squares planes, calculated by the method of Blow,[15] are given in Table VI.

Discussion

The structure exhibits noncrystallographic C_{2v}-2mm symmetry; one mirror plane passes through the ReSiRe triangle while the second relates the two Re(CO)$_4$ entities and passes through the Si atom and the center of the Re–Re bond. The deviations from these planes are small and involve only the carbonyl oxygen atoms. There are no bridging carbonyl groups. Each Re atom has, with respect to the Re–Re bond, three *equatorial* and one *axial* terminal carbonyl groups. The diphenylsilicon group bridges the Re–Re bond and lies between the two remaining *equatorial* positions which are presumed to be occupied by the hydrogen atoms. The structure is related to $Re_2(CO)_{10}$[16] and $Mn_2(CO)_{10}$[17] but unlike these exhibits an eclipsed configuration necessitated by the bridging Si atom. It resembles most closely the hydrogen-bridged anion $H_2Re_3(CO)_{12}^-$ [3] with the $H_2Re(CO)_4$ group replaced by an $H_2Si(C_6H_5)_2$ group. The Re–Re bond of 3.121 (2) Å is longer than the values of 3.02 Å in $Re_2(CO)_{10}$, 2.956 (7)–3.024 (7) Å in $Re_4(CO)_{16}^{2-}$,[18] and 3.035 (7) Å for the bond in $H_2Re_3(CO)_{12}^-$ which is not hydrogen bridged. In the latter compound the Re–Re bonds bridged by hydrogen are 3.173 (7) and 3.181 (7) Å longer than the silicon-bridged bond in the present compound. The carbonyl groups in $Re_2(CO)_{10}$ have a staggered configuration which minimizes O···O repulsive forces between the halves of the dimer. In $Re_4(CO)_{16}^{2-}$ there is a small degree of twisting about the Re–Re bonds such that overcrowding of the eclipsed carbonyl group is relieved, and there is no O···O contact less than 3.06 Å. In the present compound the minimum such contact is 2.96 (4) Å and it seems possible that the increased Re–Re length is a consequence of O···O repulsions between carbonyl groups which are *equatorial* with respect to the Re–Re bond. The bridging silicon atom apparently prevents the twisting that affords steric relief in $Re_2(CO)_{10}$ and, to a lesser extent, in $Re_4(CO)_{16}^{2-}$.

The errors in the Re–CO distances are large and the distances show considerable deviations. It is of possible significance that the two Re–CO distances where the CO is *trans* to Si are longer at 2.06 (4) and 2.08 (5) Å than the other six distances with mean value 1.92 Å (rms deviation 0.06 Å). The latter figure agrees closely with $Re_4(CO)_{16}^{2-}$ where eight Re–CO distances agree within error, mean value 1.91 (3) Å. The mean C–O distance is an unexceptional 1.16 (4) Å. The Re–C–O angles are in the range 170–179°, and the bending, which is not significant in view of the positional uncertainty of the light atoms, amounts to 5° on the average. The Si atom bridges symmetrically with Re–Si distances of 2.544 (9) Å and Re–Re–Si angles of

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52.2 (2)°. There are no comparable values in the literature; the sum of the covalent radii is 2.68 Å, using 1.51 Å for Re (from $Re_2(CO)_{10}$) and 1.17 Å for Si.[19] The angle subtended at the Si atom by the two phenyl groups is within error of the tetrahedral angle, while the Re–Si–Re angle is considerably more acute at 75.7 (3)°. If the hydrogen atoms are positioned in the plane of the ReSiRe triangle such that the Re–Re–H angle is 90°, then a Re–H length of 1.68 Å[20] gives an Si–H distance of 1.59 Å and an H–Si–H angle of 156.1°. Thus an sp^3-hybridized Si atom would have two orbitals directed toward the coordination atoms of the phenyl rings and two toward the centroids of the ReHSi triangles.

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The Structure of Pentakis(2-picoline N-oxide)cobalt(II) Perchlorate, $[Co(C_6H_7NO)_5](ClO_4)_2$

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The crystal structure of pentakis(2-picoline N-oxide)cobalt(II) perchlorate, $[Co(C_6H_7NO)_5](ClO_4)_2$, has been determined from X-ray counter data. The material crystallizes in the monoclinic space group $C_{2h}{}^5$-$P2_1/c$, with a = 18.667 (7) Å, b = 10.444 (8) Å, c = 18.665 (7) Å, β = 96° 21 (1)′, Z = 4, d_{obsd} = 1.45 (5) g/cm³, and d_{calcd} = 1.48 g/cm³. A least-squares refinement gave a final conventional R factor of 0.091 for those 1611 reflections above background with values of $\lambda^{-1} \sin \theta > 0.3$ Å^{-1}, whereas that for all 2293 independent reflections above background was 0.103. The compound consists of well-separated pentakis(2-picoline N-oxide)cobalt(II) and perchlorate ions. The immediate coordination about the cobalt atom for this d^7 high-spin complex is essentially trigonal bipyramidal with the axial Co–O bond length greater than the equatorial bond length by 0.123 (9) Å.

Introduction

Because of their simplicity five-coordinate transition metal complexes of the type MX_5 are of especial importance. Although fewer than a dozen such complexes have been characterized structurally, the results have provided important information on some of the factors which determine the resultant geometries.[1] Of those compounds so characterized, all have been low-spin d^8, d^9, or d^{10} systems. The present structural study of the five-coordinate Co(II) complex pentakis(2-picoline N-oxide)cobalt(II) perchlorate is the first such study of a high-spin d^7 complex containing the MX_5 group. On the basis of infrared and electronic spectra, Byers, Lever, and Parish,[2] who prepared the compound initially, characterized it as containing in solution trigonal-bipyramidal Co(II). We find this same geometry in the crystalline state. The comparison of this trigonal-bipyramidal, high-spin d^7 complex with those MX_5 complexes previously characterized adds useful information on the relative importance of the various factors (*e.g.*, ligand–ligand repulsion and d-electron–ligand repulsion) which determine the relative axial and equatorial bond lengths in MX_5 trigonal bipyramids.

Experimental Section

Collection and Reduction of X-Ray Data.—Violet crystals of pentakis(2-picoline N-oxide)cobalt(II) perchlorate were kindly supplied by Professor A. B. P. Lever and Dr. W. Byers. The crystals fell into two distinct habits: plates and prisms. Since the former gave X-ray photographs of a poorer quality, the structural study was carried out on one of the prisms, of approximate dimensions 0.2 × 0.2 × 0.8 mm, sealed in a glass capillary. Preliminary optical and X-ray examination indicated that the crystals belong to the monoclinic system. The systematic absences, as determined from $hk0$ and $h0l$ through $h3l$ photographs (hkl, none; $h0l$, $l = 2n + 1$; $0k0$, $k = 2n + 1$) are consistent with the space group $C_{2h}{}^5$-$P2_1/c$. The lattice parameters at 23°, obtained using Mo $K\alpha_1$ radiation (λ 0.7093 Å) are a = 18.667 (7) Å, b = 10.444 (8) Å, c = 18.665 (7) Å, and β = 96° 21 (1)′. The least-squares refinement of cell parameters was carried out as previously described.[3] The setting angles χ, ϕ, and 2θ of eight high-angle (2θ) reflections, as obtained from a narrow-source and narrow-counter aperture, were used. The density, as measured by flotation in a hexane–carbon tetrachloride mixture, of 1.45 (5) g/cm³ agrees with a value of 1.48 g/cm³ calculated for four formula units per cell. The large uncertainty in the observed density results from the rapid dissolution of the crystals in halocarbons commonly used for density measurement. Since the order of the space group is 4, no crystallographic symmetry need be imposed on the structure.

The crystal was mounted on an automatic Picker four-circle diffractometer, and the unique axis b (the 0.8-mm dimension of the crystal) was slightly offset from coincidence with the polar (ϕ) axis of the instrument, in order to decrease the probability of multiple diffraction effects.[4] At a low takeoff angle and wide counter aperture, representative peaks showed a maximum width at half-height of 0.1° in ω. Intensity data were collected as previously described using Mo $K\alpha$ radiation filtered

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