Structural Studies of Incipient Pentacoordination of Silicon in Hydrido Transition-Metal Silyl Compounds.
I. The Crystal Structure of cis-Hydridotriphenylsilyl-(η-cyclopentadienyl)dicarbonylrhenium, $(\eta^5\text{-}C_5H_5)Re(CO)_2HSi(C_6H_5)_3$

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$(\eta^5\text{-}C_5H_5)Re(CO)_2HSi(C_6H_5)_3$ is monoclinic, $P2_1/n$, $a = 13\cdot161$ (12), $b = 17\cdot502$ (17), $c = 9\cdot579$ (4) Å, $\beta = 18$ (8)°, $Z = 4$, $\rho = 1\cdot71$ g cm^{-3}. The Re compound is isomorphous with its Mn analogue, but certain differences in molecular structure are apparent: the Re—Si is considerably shorter than the Mn—Si bond when the different sizes of the metal atoms are taken into account, and the H atom bonded to the metal is ~2·2 Å from the Si for the Re as opposed to ~1·8 Å for the Mn compound. The final *R* for 1559 counter reflexions was 3·5%.

Introduction

Si has been found to show normal pentacoordination in $[(CH_3)_2NSiH_3]_5$ with trigonal-bipyramidal geometry and an average Si—N distance of 1·98 Å (Hamilton, Rudman, Novick & Goldfarb, 1967). Si—N bonds have also been claimed for the silatranes by Boer & Turley (1969). The N in the silatranes is held in place by fused-ring systems and Si—N distances range from 2·12 to 2·34 Å, but the variation in these distances in response to a change in the *trans* ligand would indicate some sort of Si—N bond. The detection of pentacoordination *per se* does not provide evidence to invoke the participation of Si $3d$ orbitals however; for example in 1-bromo-μ-trimethylsilylpentaborane(9) the Si atom has five close contacts, but the bonding in the Si—B₂ fragment is described in terms of a three-centre two-electron bond (Dahl & Calabrese, 1971).

In compounds in which a transition metal is bonded directly to Si, the coordination of the latter is best described as tetrahedral. In a few transition-metal hydride species a close approach by the H ligand to the Si atom suggests incipient pentacoordination, somewhat similar to the silatranes. Si—H distances of 1·8 and 2·0 Å were found respectively in $(\eta^5\text{-}C_5H_5)Mn(CO)_2HSi(C_6H_5)_3$ (Hutcheon, 1971) and $(\eta^5\text{-}C_5H_5)Mn(CO)_2HSiCl_2C_6H_5$ (Simpson, 1973). The crystal structure determination of the Re analogue of the former was undertaken to determine the effect of providing more room for the H atom by increasing the size of the coordination sphere while maintaining all other factors constant. The definition of *cis* needs clarification where the coordination about the central metal atom is a square pyramid. The four

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ligands forming the base are regarded as a square plane and the terminology follows from this. For the Re system both the *cis* and *trans* isomers appear to exist, although only the former has been isolated in a form suitable for diffraction studies. For the Mn compound there is no evidence for a *trans* isomer (Graham & Hoyano, 1971).

Experimental

A sample of the compound was kindly supplied by Drs W. A. G. Graham and J. K. Hoyano of this Department. Preliminary photographs indicated space group $P2_1/n$ with general positions $\pm(x, y, z; \frac{1}{2} + x, \frac{1}{2} + y, \frac{1}{2} + z)$. A fresh crystal $0\cdot15 \times 0\cdot30 \times 0\cdot35$ mm was mounted on a manual Picker diffractometer, and the intensities of 2403 reflexions with $0 \le 2\theta \le 42°$ were measured in the coupled $\omega/2\theta$ scan mode [Mo $K\alpha$ radiation, graphite (002) monochromator]. The data were reduced to $|F|$ and $\sigma(F)$ (Doedens & Ibers, 1967). Only those data (1559 observations) with $I \ge 3\sigma(I)$ were corrected for absorption (Coppens, Leiserowitz & Rabinovich, 1965) and used in subsequent calculations. The transmission factors ranged from 0·646 to 0·735 [μ(Mo $K\alpha$) = 60 cm^{-1}]. At the end of data collection several of the most intense high-angle reflexions were carefully centred in 2θ (no monochromator, Cu $K\alpha_1$ radiation, $\lambda = 1\cdot54051$ Å) and the cell dimensions obtained (see abstract).

Solution and refinement of the structure

The structure is isomorphous with the Mn analogue (Hutcheon, 1971) and the final coordinates of this

Table 1. *Results from a series of difference maps for* cis-$(\eta^5$-$C_5H_5)Re(CO)_2HSi(C_6H_5)_3$

$\sin\theta/\lambda$ cut-off	x	y	z	Re—H	Si—H	C—H	Observed electron density (e Å^{-3})
0·20	0·014	0·255	0·031	1·73 Å	2·17 Å	2·17 Å	0·16
0·25	0·005	0·258	0·036	1·62	2·20	2·05	0·26
0·30	0·005	0·265	0·028	1·66	2·29	1·99	0·35
0·35	0·005	0·260	0·011	1·68	2·02	2·12	0·38
All data	−0·001	0·272	−0·010	1·75	1·97	2·05	0·54

structure, with the exception of the H atom of interest, were used as a trial structure for the Re compound which refined smoothly to $R = 3\cdot6\%$. The scattering factors for heavy atoms were those of Cromer & Mann (1968), and for H those of Mason & Robertson (1966). The real and imaginary terms of anomalous dispersion for Re and Si were included (Ibers & Hamilton, 1964). Re and Si were treated as individual atoms and given anisotropic thermal parameters; the atoms of the carbonyl groups were treated as individual atoms, but were constrained to isotropic thermal parameters; the phenyl groups were treated as rigid bodies with C—C $= 1\cdot39$ Å (Bennett & Foxman, 1974); and the C atoms of the cyclopentadienyl group were treated as a hindered rotor (Bennett, Hutcheon & Foxman, 1975). The H atoms associated with the phenyl and cyclopentadiene rings were included at the calculated positions, assum-

Table 2. *Independent atom parameters for* cis-$(\eta^5$-$C_5H_5)Re(CO)_2HSi(C_6H_5)_3$

The standard deviations are given in parentheses and refer to the last reported digit.

Anisotropic atoms

	x	y	z
Re	−0·11317 (3)	0·24026 (2)	0·06814 (5)
Si	−0·04600 (9)	0·20190 (9)	−0·1600 (3)

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Re	0·035	0·045	0·041	0·0005	0·0025	0·0001
Si	0·038	0·038	0·040	−0·0004	0·0013	0·0023

Isotropic atoms

	x	y	z	U (Å^2)
C(1)	−0·082 (1)	0·343 (1)	0·113 (1)	0·067 (4)
O(1)	−0·058 (1)	0·408 (1)	0·138 (1)	0·081 (5)
C(2)	−0·209 (1)	0·287 (1)	−0·058 (1)	0·054 (4)
O(2)	−0·273 (1)	0·311 (1)	−0·136 (1)	0·050 (4)

Table 3. *Group parameters for* cis-$(\eta^5$-$C_5H_5)Re(CO)_2HSi(C_6H_5)_3$

The standard deviations are given in parentheses and refer to the last reported digit.

Rigid bodies

Positional parameters

Ring	x	y	z	D	E	F
1	−0·2189 (4)	0·0925 (3)	−0·3226 (5)	3·33 (1)	2·46 (1)	4·81 (1)
2	0·0126 (3)	0·3405 (3)	−0·3760 (5)	3·20 (1)	1·24 (1)	3·39 (1)
3	0·1721 (4)	0·1059 (2)	−0·1380 (6)	2·27 (1)	2·45 (1)	3·39 (1)

Hydrogen rings

4	All parameters as for ring 1
5	All parameters as for ring 2
6	All parameters as for ring 3

Thermal parameters

Ring	B_1	B_2	B_3	B_4	B_5	B_6
1	4·0 (2)	5·9 (3)	6·4 (4)	6·1 (3)	4·9 (3)	3·5 (2)
2	4·0 (2)	4·7 (3)	4·3 (3)	4·5 (3)	3·8 (2)	2·8 (2)
3	4·8 (3)	5·3 (3)	5·6 (3)	5·5 (3)	5·5 (3)	4·1 (3)
4	4·3	6·5	7·0	6·7	5·4	—
5	4·4	5·0	4·7	4·9	4·2	—
6	5·6	5·8	6·1	5·9	4·4	—

Hindered rotors

Rotor	x	y	z	B	B_d	Radius
1	−0·1404 (4)	0·1607 (3)	0·2029 (6)	4·3 (2)	3·0 (5)	1·226 (6) Å
2	−0·1392 (33)	0·1675 (24)	0·1996 (45)	2·5 (14)	3·5 (20)	2·16 (4)

	D	E	F
1	2·32 (1)	2·87 (1)	2·49 (1)
2		Constrained to be as above.	

ing that they were coplanar with the rings, with C—H = 1·0 Å.

A difference map computed with all the data contained features of magnitude ±0·6 e Å^{-3} in the vicinity of the Re atom; elsewhere in the map the features were of the order ±0·3 e Å^{-3}. The second largest feature of this map was in a reasonable position for the one atom omitted from the model, but this alone does not provide sufficient evidence for the assignment of a H atom to a peak so close to a third transition-series element when the largest residual peak is ignored. A more rigorous assessment of the nature of the peak involves the calculation of several electron density maps and changing the upper $\sin\theta/\lambda$ limit of the contributing data (La Placa & Ibers, 1965). Peak positions were determined (Booth, 1948) and the results are shown in Table 1.

The peak that is most reasonably assigned to the H is found to be the largest feature in all maps with a maximum $\sin\theta/\lambda$ limit of 0·35. The largest peak of the map computed with all the data appears to arise from the high-angle data, and is more likely to be a result of errors in the thermal parameters. The inclusion of this H atom reduced R to 3·5%. When its parameters were allowed to vary in least-squares refinement they stayed within one standard deviation of the coordinates obtained from the difference maps and thus satisfied some criticisms made by Huber-Buser (1971). The H atom can be assigned, tentatively, to a location approximately 1·7 Å from the Re atom and with non-bonded contacts to Si and C of approximately 2·2 and 2·1 Å respectively.

Results

Table 2 contains the final atomic parameters for the independent atoms; the atomic coordinates, derived from the group parameters in Table 3, are collected in Table 4. Tables 5 and 6 list pertinent intramolecular angles and distances respectively. Fig. 1 depicts a skeletal view of the core of the compound seen down the vector from
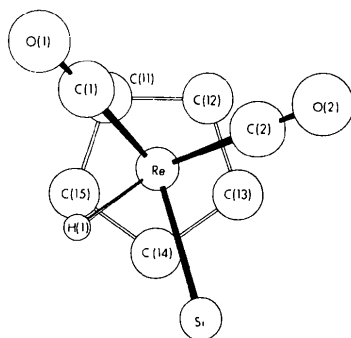
Table 4. Parameters derived from groups in $(\eta^5\text{-}C_5H_5)Re(CO)_2HSi(C_6H_5)_3$

The standard deviations are given in parentheses and refer to the last reported digit. The H atoms are labelled with the same number as the C atoms to which they are attached.

	x	y	z
C(21)	−0·2139 (7)	0·1702 (3)	−0·3524 (9)
C(22)	−0·2884 (6)	0·1250 (5)	−0·4185 (7)
C(23)	−0·2934 (6)	0·0473 (4)	−0·3884 (7)
C(24)	−0·2239 (7)	0·0148 (3)	−0·2928 (9)
C(25)	−0·1494 (6)	0·0599 (5)	−0·2270 (7)
C(26)	−0·1444 (6)	0·1376 (5)	−0·2568 (7)
C(31)	−0·0197 (6)	0·3596 (4)	−0·2437 (5)
C(32)	0·0085 (6)	0·4167 (3)	−0·3357 (7)
C(33)	0·0409 (6)	0·3975 (4)	−0·4679 (7)
C(34)	0·0451 (6)	0·3213 (4)	−0·5081 (6)
C(35)	0·0168 (6)	0·2641 (3)	−0·4161 (7)
C(36)	−0·0155 (6)	0·2833 (4)	−0·2839 (6)
C(41)	0·1041 (9)	0·0946 (5)	−0·2509 (9)
C(42)	0·1975 (9)	0·0571 (4)	−0·2509 (9)
C(43)	0·2654 (9)	0·0684 (5)	−0·1330 (8)
C(44)	0·2400 (9)	0·1172 (5)	−0·0249 (9)
C(45)	0·1467 (9)	0·1574 (4)	−0·0299 (9)
C(46)	0·0787 (9)	0·1434 (5)	−0·1429 (8)
H(21)	−0·2103	0·2263	−0·3741
H(22)	−0·3385	0·1484	−0·4874
H(23)	−0·3471	0·0146	−0·2710
H(24)	−0·2275	−0·0413	−0·2710
H(25)	−0·0993	0·0365	−0·1578
H(31)	−0·0431	0·3734	−0·1482
H(32)	0·0054	0·4718	−0·3065
H(33)	0·0611	0·4388	−0·5341
H(34)	0·0683	0·3074	−0·6035
H(35)	0·0197	0·2090	−0·4452
H(41)	0·0551	0·0864	−0·3325
H(42)	0·2158	0·0218	−0·3238
H(43)	0·3327	0·0413	−0·1292
H(44)	0·2889	0·1254	0·0566
H(45)	0·1282	0·1900	0·0479
C(11)	−0·1382 (9)	0·2072 (5)	0·2981 (9)
C(12)	−0·2266 (9)	0·1853 (6)	0·2151 (9)
C(13)	−0·1959 (9)	0·1294 (5)	0·1152 (9)
C(14)	−0·0886 (9)	0·1167 (5)	0·1366 (8)
C(15)	−0·0529 (9)	0·1649 (6)	0·2496 (9)
H(11)	−0·135 (3)	0·164 (5)	0·368 (4)
H(12)	−0·291 (3)	0·211 (2)	0·221 (4)
H(13)	−0·237 (3)	0·112 (2)	0·045 (5)
H(14)	−0·048 (3)	0·090 (2)	0·082 (4)
H(15)	0·015 (3)	0·175 (2)	0·282 (4)

Fig. 1. A skeletal view of the core of the cis-hydridotriphenylsilyl-(cyclopentadienyl)dicarbonylrhenium molecule viewed down the vector from the Re atom to the centre of the C$_5$ ring.
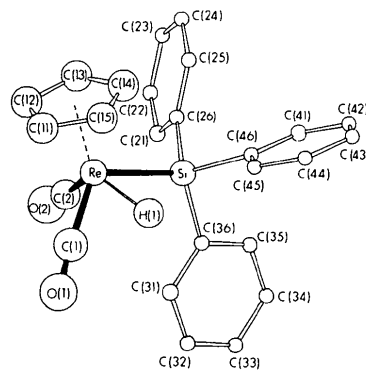

Fig. 2. A perspective view of the cis-hydridotriphenylsilyl(cyclopentadienyl)dicarbonylrhenium molecule.

Table 5. *Interatomic angles in*
$(\eta^5\text{-}C_5H_5)Re(CO)_2HSi(C_6H_5)_3$

C(1)—Re—C(2)	83·5 (5)°	Re—Si—C(46)	113·8 (3)°
C(1)—Re—Si	112·9 (4)	Cpd*—Re—Si	116·7 (5)
C(2)—Re—Si	78·8 (4)	Cpd—Re—C(1)	125·4 (5)
Re—Si—C(26)	109·5 (3)	Re—C(1)—O(1)	177·0 (9)
Re—Si—C(36)	115·1 (3)	Re—C(2)—O(2)	175·8 (9)

* Cyclopentadienyl ring.

Table 6. *Intramolecular distances in*
$(\eta^5\text{-}C_5H_5)Re(CO)_2HSi(C_6H_5)_3$

(a) Bonded

Re—Si	2·49 (1) Å	Si—C(26)	1·93 (1) Å
Re—C(1)	1·87 (1)	Si—C(36)	1·91 (1)
Re—C(2)	1·89 (1)	Si—C(46)	1·94 (1)
Re—C(11)	2·32 (1)	C(11)—C(12)	1·44 (1)
Re—C(12)	2·31 (1)	C(1)—O(1)	1·19 (1)
Re—C(13)	2·30 (1)	C(2)—O(2)	1·16 (1)
Re—C(14)	2·31 (1)	Re—H(1)	~1·66
Re—C(15)	2·32 (2)		

(b) Non-bonded

| C(1)···C(2) | 2·50 (1) Å | C(2)···H(1) | ~1·99 Å |
| Si···C(2) | 2·82 (1) | Si···H(1) | ~2·19 |

the Re atom to the centre of the cyclopentadienyl ring, and Fig. 2 a perspective view of the whole molecule.*

Discussion

There is little difference between the Re and Mn compounds. However, while they are isomorphous they are not quite isostructural. The differences are small, but consistent with the significant differences in the positioning of the H atom bonded to the metal.

Re—Si at 2·49 (1) Å is only 0·07 (1) Å longer than the equivalent Mn—Si distance, whereas the distances from the centre of the cyclopentadienyl ring to the Re and Mn atoms, 1·96 (1) and 1·79 (1) Å respectively, indicate a difference of 0·17 (1) Å in covalent radii (Barbeau, Dichmann & Ricard, 1973). The difference between Re—Si and Mn—Si in $M_2(CO)_8[Si(C_6H_5)_2]_2$, $M = Re$ (Cowie, 1974), $M = Mn$ (Simon & Dahl, 1973), is 0·14, only 0·03 Å different from the covalent radii.

One expected effect of changing the transition metal (M) from Re to Mn in compounds of the type (η^5-$C_5H_5)M(CO)_2HSi(C_6H_5)_3$ would be a reduction in interligand non-bonded repulsions because of the increase in size of the central metal atom and a concomi-

tant increase in metal–ligand bond lengths. While this is generally true, the non-bonded C···C contacts between the two carbonyl groups in each molecule are remarkably similar (2·50 for Re and 2·48 Å for Mn). This constancy coupled with the difference in M—C distances results in a marked difference in OC—$\hat{M}$—CO angles (83·5 for Re, 89·7° for Mn). The net effect of the angular and bond-length changes in going from Mn to Re is to produce more space for the H ligand. The extremely short Si···H contact ($\leq 2·0$ Å) in $(\eta^5$-$C_5H_5)$-$Mn(CO)_2HSi(C_6H_5)_3$ and $(\eta^5$-$C_5H_5)Mn(CO)_2HSiCl_2$-C_6H_5 (Hutcheon, 1971; Simpson, 1973) does not appear to be present in the Re compound.

Since the direct location of the H ligand is less certain in $(\eta^5$-$C_5H_5)Re(CO)_2HSi(C_6H_5)_3$, the possible positions were examined by minimizing intramolecular non-bonded contacts. Three repulsive non-bonded contacts [C(1)···H, Si···H and H(45)···H] appear to be sensitive to the H location. Table 7 contains these contacts calculated for a range of H positions. The angles (θ, ϕ) in this table are the polar coordinates. The positive z direction (*i.e.* $\theta = 0$) was defined by the vector from the Re atom to the centre of the cyclopentadienyl ring, the Re—C(1) vector was defined as having $\phi = 0$, and the Re—H distance was assumed to be 1·68 Å (Churchill & Bau, 1967; Abrahams, Ginsberg & Knox, 1964). The data in Table 7 show the definite trends: (1) for θ constant, C(1)···H increases with increasing ϕ while Si···H and H(45)···H both decrease; and (2) for ϕ constant, C(1)···H and Si···H increase with increasing θ while H(45)···H decreases. Since all contacts in this table can be judged to be repulsive (Pauling, 1960), an increase in the contact distance corresponds to a decrease in the repulsion. The position of the H ligand determined from the

Table 7. *Hydride–other atom contacts* (Å) *for a series of hydride-atom locations*

$\theta = 120°$

$\phi(°)$	75	80	85	90	95	100
C(1)—H	1·72	1·82	1·93	2·03	2·12	2·21
Si—H	2·45	2·34	2·22	2·10	1·98	1·85
H(45)—H	2·16	2·10	2·05	2·01	1·99	1·99

$\theta = 115°$

$\phi(°)$	75	80	85	90	95	100
C(1)—H	1·78	1·89	1·99	2·10	2·18	2·28
Si—H	2·50	2·38	2·26	2·14	2·01	1·88
H(45)—H	2·07	2·00	1·94	1·91	1·88	1·88

$\theta = 110°$

$\phi(°)$	75	80	85	90	95	100
C(1)—H	1·85	1·95	2·06	2·16	2·25	2·34
Si—H	2·55	2·43	2·31	2·18	2·05	1·93
H(45)—H	1·99	1·92	1·86	1·82	1·80	1·80

The favoured position for the H atom is
$\theta = 115 \pm 5°$
$\phi = 85 \pm 5°$.

difference maps corresponds to $\phi = 85°$ and $\theta = 115°$, and is at the position that would be predicted from the data in Table 7. This position seems to represent a reasonable minimum of the repulsions when the observed non-bonded $C \cdots H$ contacts in the Mn derivative and $H \cdots H$ in the work of Bailey & Mason (1966) are taken into consideration. A quantitative theoretical treatment is not feasible since it would require a very accurate calculation of molecular energies.

The important structural differences between $(\eta^5\text{-}C_5H_5)M(CO)_2HSi(C_6H_5)_3$ $(M = \text{Mn or Re})$ are concerned with the M–Si bond and the $Si \cdots H$ contact. Mn–Si appears to be considerably weaker than Re–Si and it is difficult (if not impossible) to separate the contributing factors: (1) weakening of Mn–Si to offset a very repulsive $Si \cdots H$ interaction; and (2) weakening of Mn–Si by incipient pentacoordination, $i.e.$ the short $Si \cdots H$ contact (~ 1.8 Å) represents a weak bond in the Mn derivative. (1) and (2) are mutually exclusive and involve the nature of the $Si \cdots H$ interaction. Unfortunately, all steric arguments that can be used to distinguish these possibilities are based on comparison which would have an unsound statistical basis. For example, the near equivalence of $Si \cdots H$ contacts in $(\eta^5\text{-}C_5H_5)Mn(CO)_2HSiCl_2C_6H_5$ and $(\eta^5\text{-}C_5H_5)Mn(CO)_2HSi(C_6H_5)_3$ (Simpson, 1973; Hutcheon, 1971) would tend to favour the idea of a repulsive $Si \cdots H$ contact, since the more electronegative substituents of the dichlorophenylsilyl ligand might be expected to promote a $Si \cdots H$ bond and hence shorten the $Si \cdots H$ contact if it were attractive. However, the H atoms in these two Mn structures are not located with sufficient precision to allow meaningful discussion. Further discussion will appear in the following paper.

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