Crystal and Molecular Structure of Tricarbonyl[(trimethylsilyl)-π-cyclopentadienyl]rhenium

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Crystals of the title compound are monoclinic, $a = 6{\cdot}716(2)$, $b = 15{\cdot}303(3)$, $c = 27{\cdot}328(5)$ Å, $\beta = 103{\cdot}24(4)°$, $Z = 8$, space-group $P2_1/c$, two molecules per asymmetric unit. The structure was determined by Patterson and Fourier syntheses from diffractometer data and refined by full-matrix least-squares calculations to R 0·095 for 2460 observed reflections. The co-ordination around the central Re atom is octahedral, the OC–Re–CO angles ranging from 88 to 93(1·5)°. The Re–C(carbonyl) distances are 1·81—1·91(4) Å and the Re–C–O angles 172—177(3)°. The distance from the rhenium atom to the centre of the (trimethylsilyl)cyclopentadienyl ring is 1·95(4) Å. The individual, Re–C(ring) distances are 2·26—2·40 Å, mean 2·30(4) Å.

THE reaction[1] of (trimethylsilyl)(trimethylstannyl)cyclopentadiene and bromopentacarbonylrhenium yields tricarbonyl[(trimethylsilyl)-π-cyclopentadienyl]rhenium, with no trace of the organotin analogue [equation (1)].

$$(Me_3Si)(Me_3Sn)C_5H_4 + Re(CO)_5Br \longrightarrow (Me_3Si\text{-}\pi\text{-}C_5H_4)Re(CO)_3 + 2CO + Me_3SnBr \quad (1)$$

The ^1H n.m.r. spectrum of this compound has a particular feature of interest, in that the ring protons are a sharp singlet and no splitting takes place on cooling. This type of effect, which occurs in (trimethylsilyl)cyclopentadiene, has been explained[2] in terms of a temperature-dependent migration of the hydrogen atom about the C_5H_5 ring in a series of 1,3-shifts, at such a rate that apparent proton equivalence results. It seemed possible that the molecule might have an unusual structure, and a crystal-structure analysis was carried out to investigate this possibility, and to add some structural data to the very scanty Re–π-C_5H_5 structural information presently available.

EXPERIMENTAL

Crystals of $Re(CO)_3(C_5H_4SiMe_3)$ are transparent, thin plates, elongated along a with well-developed {010} and {001}. The space-group and initial unit-cell parameters were determined from Weissenberg and precession photographs, accurate unit-cell parameters being obtained later by a least-squares treatment of 22 $\sin^2\theta(hkl)$ values measured on a General Electric XRD 6 diffractometer.

Crystal Data.—$C_{11}H_{13}O_3ReSi$, $M = 407{\cdot}5$, Monoclinic, $a = 6{\cdot}716(2)$, $b = 15{\cdot}303(3)$, $c = 27{\cdot}328(5)$ Å, $\beta = 103{\cdot}24(4)°$, $U = 2733{\cdot}9$ Å^3, $D_m = 2{\cdot}00$ (flotation), $Z = 8$, $D_c = 1{\cdot}98$. Mo-K_α radiation, $\lambda = 0{\cdot}71069$ Å; μ(Mo-K_α) = 95 cm^{-1}. Space-group $P2_1/c$ (C_{2h}^5) from absence spectra: $h0l$, l odd; $0k0$, k odd.

Intensity data were collected on a Datex-automated General Electric XRD 6 diffractometer using a θ—2θ scan at 2° min^{-1} in 2θ. All reflections with $2\theta(\text{Mo-}K_\alpha) \leqslant 45°$ were measured. Of the 3494 independent reflections, 1027 had intensities $< 3\sigma(I)$ above background, where $\sigma(I)$ is defined by: $\sigma^2(I) = S + B + (0{\cdot}05S)^2$, where S = scan count, B = background. These reflections were classified as unobserved. A check scaling reflection was monitored

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[1] E. W. Abel and S. Moorhouse, *J. Organometallic Chem.*, 1971, **29**, 227.

[2] C. S. Kraihanzel and M. L. Losee, *J. Amer. Chem. Soc.*, 1968, **90**, 4701.

every 30 reflections; its intensity had fallen off by 11% of its starting value at the end of the data collection. Lorentz and polarization corrections were applied and the structure amplitudes were derived. Crystal dimensions were 0·4 × 0·2 × 0·4 mm.

Structure Determination and Refinement.—The positions of the two independent rhenium atoms in the asymmetric unit were determined from a three-dimensional, unsharpened Patterson synthesis. Two cycles of full-matrix least-squares refinement of these positions and a scale-factor (with a constant isotropic B of 3·0 Å^2), gave R 0·25. A subsequent three-dimensional Fourier summation resolved the remainder of the two molecules, excluding hydrogen atoms. Refinement proceeded with full-matrix least-squares calculations, the rhenium and silicon atoms having anisotropic temperature factors of the form: $f = f^0 \exp -(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)$, where f^0 is the tabulated [3] scattering factor (that of Re being corrected for the real and imaginary components of anomalous dispersion [4]), and f is the value corrected for thermal motion; the carbon and oxygen atoms were assigned isotropic temperature factors. At this stage R was 0·13. An absorption correction [5] was then applied to the data and the R fell to 0·10. Seven reflections, thought to be suffering from extinction errors (020, 021, 032, 042, 110, 132, 152) were given zero weight in the final cycles of refinement. A weighting scheme of the form, $w = [1 + (|F_o| - 60)^2/30^2]^{-1}$, was used in the final stages of refinement and also before applying the absorption correction. Its usefulness was confirmed from an analysis of $w(|F_o| - |F_c|)^2$, average values of which over ranges of $|F_o|$ were approximately constant. The unobserved reflections were given zero weight in the refinement. Convergence was reached at R 0·095 for the 2460 reflections used in the refinement, and no parameter shift in the final cycle was $>0·5\sigma$. The final positional and thermal parameters are given in Table 1. Measured and calculated structure-factors are listed in Supplementary Publication No. SUP 20298 (7 pp., 1 microfiche).*

DISCUSSION

The Figure shows the two independent molecules of $Re(CO)_3(C_5H_4SiMe_3)$ in the asymmetric unit viewed down a^*. Bond lengths and angles, with their standard deviations are listed in Table 2. There are no real differences between the bond lengths and angles of either molecule so that mean values will be taken over both.

The Re–C(carbonyl) distances, ranging from 1·81 to 1·91 Å, mean 1·86(4) Å, compare quite well with the corresponding mean distances in $[Re(CO)_3SMe]_4$, 1·87(5),[6] $[Bu^n{}_4N]_2[Re_4(CO)_{16}]$, 1·91(4),[7] and $HRe_2Mn(CO)_{11}$, 1·95(3) Å.[8] The Re–C–O grouping, angles 172—177(3)°, are linear within experimental error, although significant deviations from linearity often occur in metal carbonyls, and can be explained [9,10] on the basis of simple MO considerations. The co-ordination around the central rhenium atom is octahedral, the OC–Re–CO angles varying from 88 to 93(1·5)°.

TABLE 1

Final positional parameters (fractional ×10^4) and thermal parameters (B and $10^4\beta_{ij}$), with standard deviations in parentheses

Atom	x	y	z	B/Å^2
Molecule (1)				
Re(1)	1148(2)	1345(1)	637(0)	
Si(1)	3698(16)	3402(6)	391(4)	
O(1)	−954(40)	2409(17)	1318(9)	6·41(54)
O(2)	−2364(44)	1740(20)	−285(10)	7·33(60)
O(3)	−935(40)	−330(18)	835(9)	6·74(56)
C(1)	−155(53)	2031(23)	1058(12)	5·11(68)
C(2)	−909(64)	1579(28)	70(15)	6·54(85)
C(3)	−45(54)	341(24)	773(12)	5·36(68)
C(7)	4345(59)	1817(26)	1049(14)	6·17(80)
C(8)	3824(42)	2201(18)	546(10)	3·64(52)
C(9)	3725(54)	1475(23)	233(12)	5·23(70)
C(10)	3961(68)	650(31)	475(16)	7·69(98)
C(11)	4487(62)	916(29)	997(15)	6·92(88)
C(17)	2801(86)	4036(41)	895(20)	9·97(135)
C(18)	6163(92)	3913(43)	351(22)	11·02(151)
C(19)	1577(72)	3569(30)	−201(17)	7·69(102)
Molecule (2)				
Re(2)	1612(2)	2347(1)	3181(0)	
Si(2)	−1493(15)	395(6)	2679(3)	
O(4)	4722(48)	1084(22)	3759(11)	8·21(68)
O(5)	3563(50)	2290(22)	2286(12)	8·73(75)
O(6)	4425(42)	3827(18)	3669(10)	6·86(58)
C(4)	3522(55)	1526(23)	3509(13)	5·24(69)
C(5)	2865(44)	2314(19)	2657(10)	3·69(52)
C(6)	3347(53)	3248(23)	3466(12)	5·17(67)
C(12)	−1009(55)	1729(24)	3461(12)	5·44(69)
C(13)	−1429(48)	1473(20)	2940(11)	4·43(61)
C(14)	−1577(47)	2360(21)	2670(11)	4·36(58)
C(15)	−1556(73)	3005(31)	3059(17)	8·00(105)
C(16)	−1097(63)	2688(27)	3510(15)	6·43(84)
C(20)	222(69)	−358(30)	3107(16)	7·87(102)
C(21)	−4220(76)	−8(32)	2572(17)	8·52(111)
C(22)	−725(58)	470(24)	2055(13)	5·99(76)

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Re(1)	2524(40)	328(6)	160(2)	−151(11)	274(6)	4(3)
Si(1)	5674(354)	647(47)	388(23)	−459(106)	470(69)	25(26)
Re(2)	2257(38)	363(6)	185(2)	21(11)	242(6)	−51(3)
Si(2)	3470(281)	392(40)	176(15)	−212(87)	359(50)	−27(19)

The interesting feature of the structure is the co-ordination of the rhenium to the (trimethylsilyl)cyclopentadiene moiety. The only reported X-ray study of a (π-cyclopentadienyl)rhenium complex seems to be that of $(C_5H_5)Re(Me)_2(C_5H_5Me)$,[11] where the co-ordination around the rhenium is distorted octahedral, the Me–Re–Me angle being 76°, compared to an average value of 90° for OC–Re–CO angles in the present study.

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* For details of Supplementary Publications see Notice to Authors No. 7 in *J. Chem. Soc.* (*A*), 1970, Issue No. 20 (items less than 10 pp. will be sent as full-size copies).

[3] 'International Tables for X-Ray Crystallography,' vol. III, Kynoch Press, Birmingham, 1962, p. 202—207.

[4] Ref. 3, p. 215.

[5] P. Coppens, L. Leiserowitz, and D. Rabinovich, *Acta Cryst.*, 1965, **18**, 1035.

[6] E. W. Abel, W. Harrison, R. A. N. McLean, W. C. Marsh, and J. Trotter, *Chem. Comm.*, 1970, 1531.

[7] M. R. Churchill and R. Bau, *Inorg. Chem.*, 1968, **7**, 2606.

[8] M. R. Churchill and R. Bau, *Inorg. Chem.*, 1967, **6**, 2086.

[9] S. F. A. Kettle, *Inorg. Chem.*, 1965, **4**, 1661.

[10] S. F. A. Kettle, *Inorg. Chem.*, 1965, **4**, 1821.

[11] N. W. Alcock, *J. Chem. Soc.* (*A*), 1967, 2001.

The rhenium–ring centre is 1·89(4) Å in $(C_5H_5)Re(Me)_2(C_5H_5Me)$ and 1·95(4) Å (Table 3) in $Re(CO)_3(C_5H_4SiMe_3)$, and the individual Re–C(ring) distances range from 2·16 to 2·34, mean 2·25(4) Å in the former, and 2·26 to 2·40, mean 2·30(4) Å in the latter. In both structures the variations among the individual values are probably not significant, and both mean values compare favourably with the predicted value of 2·25 Å for a Re–C(sp^2) bond, taking 1·51 Å as the covalent radius of rhenium.[12] The observed lengths of the C–C bonds vary from 1·30 to 1·54 Å, but with rather large standard deviations (Table 2), and the differences are not significant, the mean value being 1·43 Å. The dihedral angle between the mean plane of the $C_5H_4SiMe_3$ ring and the plane determined by the carbonyl carbons is 2·9 and 0·5° respectively for molecules (1) and (2). These differences are not significant and for all purposes the planes are parallel.

TABLE 2

Bond distances (Å) and angles (°), with standard deviations in parentheses

(*a*) Distances

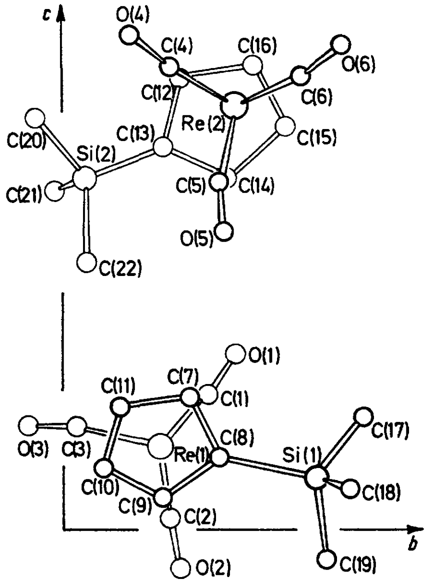
Molecule (1)		Molecule (2)	
Re(1)–C(1)	1·91(3)	Re(2)–C(4)	1·87(4)
Re(1)–C(2)	1·86(4)	Re(2)–C(5)	1·82(3)
Re(1)–C(3)	1·81(4)	Re(2)–C(6)	1·86(3)
Re(1)–C(7)	2·30(4)	Re(2)–C(12)	2·28(4)
Re(1)–C(8)	2·28(3)	Re(2)–C(13)	2·40(3)
Re(1)–C(9)	2·26(3)	Re(2)–C(14)	2·27(3)
Re(1)–C(10)	2·30(4)	Re(2)–C(15)	2·31(4)
Re(1)–C(11)	2·33(4)	Re(2)–C(16)	2·27(4)
Si(1)–C(8)	1·88(3)	Si(2)–C(13)	1·79(3)
Si(1)–C(17)	1·89(6)	Si(2)–C(20)	1·84(4)
Si(1)–C(18)	1·86(6)	Si(2)–C(21)	1·89(5)
Si(1)–C(19)	1·91(4)	Si(2)–C(22)	1·89(4)
C(1)–O(1)	1·14(4)	C(4)–O(4)	1·15(4)
C(2)–O(2)	1·23(4)	C(5)–O(5)	1·21(4)
C(3)–O(3)	1·22(4)	C(6)–O(6)	1·20(4)
C(7)–C(8)	1·46(4)	C(12)–C(13)	1·44(4)
C(7)–C(11)	1·39(6)	C(12)–C(16)	1·48(5)
C(8)–C(9)	1·39(4)	C(13)–C(14)	1·54(4)
C(9)–C(10)	1·42(5)	C(14)–C(15)	1·45(5)
C(10)–C(11)	1·45(5)	C(15)–C(16)	1·30(5)

	Range	Mean
Re–C (ring)	2·26—2·40	2·30
Re–C (CO)	1·81—1·91	1·86
Si–C	1·79—1·91	1·87
C–C	1·30—1·54	1·43
C–O	1·14—1·23	1·19

(*b*) Angles

Molecule (1)		Molecule (2)	
C(1)–Re(1)–C(2)	92·3(1·6)	C(4)–Re(2)–C(5)	88·2(1·4)
C(1)–Re(1)–C(3)	93·3(1·5)	C(4)–Re(2)–C(6)	90·1(1·5)
C(2)–Re(1)–C(3)	93·2(1·7)	C(5)–Re(2)–C(6)	89·5(1·4)
C(8)–Si(1)–C(17)	110(2)	C(13)–Si(2)–C(20)	112(2)
C(8)–Si(1)–C(18)	115(2)	C(13)–Si(2)–C(21)	107(2)
C(8)–Si(1)–C(19)	108(2)	C(13)–Si(2)–C(22)	108(2)
C(17)–Si(1)–C(18)	105(3)	C(20)–Si(2)–C(21)	110(2)
C(17)–Si(1)–C(19)	104(2)	C(20)–Si(2)–C(22)	110(2)
C(18)–Si(1)–C(19)	113(2)	C(21)–Si(2)–C(22)	110(2)
Re(1)–C(1)–O(1)	177(3)	Re(2)–C(4)–O(4)	172(3)
Re(1)–C(2)–O(2)	176(3)	Re(2)–C(5)–O(5)	175(3)
Re(1)–C(3)–O(3)	176(3)	Re(2)–C(6)–O(6)	177(3)
C(8)–C(7)–C(11)	108(3)	C(13)–C(12)–C(16)	111(3)
Si(1)–C(8)–C(7)	126(2)	Si(2)–C(13)–C(12)	129(2)
Si(1)–C(8)–C(9)	130(2)	Si(2)–C(13)–C(14)	129(2)
C(7)–C(8)–C(9)	103(3)	C(12)–C(13)–C(14)	102(3)
C(8)–C(9)–C(10)	116(3)	C(13)–C(14)–C(15)	105(3)
C(9)–C(10)–C(11)	101(4)	C(14)–C(15)–C(16)	114(4)
C(10)–C(11)–C(7)	112(4)	C(15)–C(16)–C(12)	107(4)

		Range	Mean
(CO)	C–Re–C	88·2—93·3	90·3
(Ring)	C–Re–C	32·9—38·3	36·0
	C–Si–C	104—115	109
	Re–C–O	172—177	176
	Si–C–C	126—130	129
	C–C–C	101—116	108



View of the two independent molecules in the asymmetric unit down *a**

TABLE 3

Equations of some weighted least-square planes in the form $lX' + mY + nZ' - p = 0$, where X, Y, and Z are in Å referred to axes a, b, and c^*; values of Δ, the deviation (Å) of atoms from the plane, are given in square brackets followed by the value of Δ/σ

	l	*m*	*n*	*p*
Plane (1): C(7)—(11)	−0·9974	−0·0717	−0·0121	2·4901
[C(7) 0·002, 0·05; C(8) 0·010, 0·36; C(9) −0·029, 0·78; C(10) 0·047, 1·00; C(11) −0·025, 0·60; Si(1) −0·128, 11·3; Re(1) 1·951]				
Plane (2): C(12)—(16)	−0·9968	−0·0424	−0·0677	−2·1276
[C(12) −0·029, 0·79; C(13) 0·037, 1·13; C(14) −0·041, 1·26; C(15) 0·076, 1·52; C(16) −0·011, 0·25; Si(2) 0·035, 3·41; Re(2) −1·948]				
Plane (3): C(7)—(11), Si(1)	−0·9993	−0·0325	−0·0202	2·4227
[C(7) 0·016, 0·41; C(8) 0·060, 2·04; C(9) −0·017, 0·47; C(10) 0·004, 0·08; C(11) −0·064, 1·50; Si(1) −0·004, 0·40; Re(1) 1·949]				
Plane (4): C(12)—(16), Si(2)	−0·9974	−0·0321	−0·0642	−2·1951
[C(12) −0·035, 0·93; C(13) 0·023, 0·70; C(14) −0·044, 1·35; C(15) 0·087, 1·75; C(16) 0,0; Si(2) 0·001, 0·09; Re(2) 1·947]				

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[12] R. J. Doedens and L. F. Dahl, *J. Amer. Chem. Soc.*, 1965, **87**, 2576.

There are no significant variations in the Si–C(Me), 1·84—1·91, mean 1·88 Å, or Si–C(ring) distances, 1·79, 1·88, mean 1·84 Å, and the mean values are in good agreement with the average value of 1·865 Å for a number of alkylsilanes and with the value of 1·84 Å in $PhSiH_3$.[13]

The crystal structure does not throw any light on the interpretation of the ^1H n.m.r. spectrum. The molecule appears to be a normal complex with the Re atom symmetrically bonded to the π-cyclopentadienyl ring.

The closest intermolecular approaches are 3·19 for C···O contacts, and 3·70 Å for C···C contacts, which indicate that the intermolecular forces are of the van der Waals type.

We thank Drs. E. W. Abel and S. Moorhouse for suggesting the problem and supplying the crystals, the National Research Council of Canada for financial support, and the staff of the University of British Columbia Computing Centre for assistance.

[1/2035 *Received, 1st November*, 1971]

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[13] *Chem. Soc. Special Publ.*, No. 11, 1958, and No. 18, 1965.