Crystal and Molecular Structure of μ-Trimethylsilylcycloheptatrienylpentacarbonyltrimethylsilyldiruthenium(*Ru–Ru*): A Binuclear Metal Complex with a Bridging Cycloheptatrienyl Ligand

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Crystals of the title compound are orthorhombic, space group $P2_12_12_1$, with $Z = 4$ in a unit cell of dimensions: $a = 10{\cdot}355(2)$, $b = 12{\cdot}380(5)$, $c = 17{\cdot}580(5)$ Å. The structure was determined by direct methods from diffractometer data and refined to R 0·049 for 2024 independent reflections. The two ruthenium atoms are bonded to one another [Ru–Ru 2·937(2) Å] and to the cycloheptatrienyl ring; four of the carbon ring atoms effectively comprise a diene system bonded (somewhat asymmetrically) to Ru(1), while the other three carbon atoms form an allyl group bonded to Ru(2). The interplanar angle between the diene and allyl fragments is 57°. The central chain of the molecule comprises the sequence OC–Ru–Ru–SiMe$_3$; the O–C–Ru–Ru chain is almost linear, but the silyl group is bent away from the C_7 ring to give Ru–Ru–Si 173° [Ru–Si 2·456(4) Å]. The two equatorial carbonyl groups on each Ru atom are approximately orthogonal to one another and are in an eclipsed configuration.

BRIDGING cycloheptatrienyl complexes may be formed[1] by the reaction of cyclohepta-1,3,5-triene or of its 7-substituted derivatives with $[\{Ru(CO)_4(SiMe_3)\}_2]$. Crystals of the title compound were formed as a minor product in a reaction which used unsubstituted cycloheptatriene as the starting material; the structural results therefore not only establish the molecular configuration of the product but also show that migration of a trimethylsilyl group from the metal to the ring must have occurred during the formation of the compound.

EXPERIMENTAL

Crystals of $[Ru_2(CO)_5(SiMe_3)(C_7H_6SiMe_3)]$ grow as orange prisms. Diffracted intensities were collected from a crystal of dimensions 0·37 × 0·25 × 0·85 mm on a Syntex $P2_1$ four-circle diffractometer according to methods described earlier.[2] Of the total 2680 reflections (complete for $3{\cdot}7° < 2\theta < 50{\cdot}0°$), 2024 were deemed 'observed' according to the criterion $I > 2{\cdot}5\sigma(I)$.

RESULTS

Crystal Data.—$C_{18}H_{24}O_5Ru_2Si_2$, $M = 578{\cdot}5$, Orthorhombic, $a = 10{\cdot}355(2)$, $b = 12{\cdot}380(5)$, $c = 17{\cdot}580(5)$ Å, $Z = 4$, $D_c = 1{\cdot}70$ g cm^{-3}, $D_m = 1{\cdot}67$ g cm^{-3}, $F(000) = 1152$. Space group $P2_12_12_1$. Mo-K_α X-radiation (graphite monochromator), $\lambda = 0{\cdot}71069$ Å; $\mu(\text{Mo-}K_\alpha) = 13{\cdot}2$ cm^{-1}.

The structure was solved by direct methods,[3] and in the final refinement (by full-matrix least-squares) anisotropic thermal parameters were used for the two ruthenium and the two silicon atoms only. Weights were applied according to the scheme $1/w = \sigma(F)^2$. Hydrogen atoms were incorporated at positions estimated from the electron-density maps, but neither their positional nor thermal parameters were refined. The refinement converted to R 0·049 (R' 0·058), and a final electron-density synthesis showed no peaks $>0{\cdot}8$ or $<-0{\cdot}6$ eÅ^{-3}. Bond lengths and angles with their respective standard deviations were computed from the variance-covariance matrix obtained in the last refinement cycle. Positional and thermal parameters are in Table 1, interatomic distances in Table 2, and some torsion angles in Table 3. No absorption correction was applied, and the atomic scattering factors used were those of ref. 4. All computational work was carried out at the University of London Computing Centre with the 'X-Ray System' of programs.[3] Observed and calculated structure factors, together with the hydrogen atom parameters, are listed in Supplementary Publication No. SUP 21151 (12 pp., 1 microfiche).*

TABLE 1

Atomic positional and thermal parameters with standard deviations in parentheses*

Atom	x/a	y/b	z/c	10^2U/Å^2
Ru(1)	0·75220(9)	0·29192(7)	0·12915(5)	†
Ru(2)	0·72649(9)	0·12561(7)	0·24734(5)	†
Si(1)	0·7569(4)	0·4454(3)	0·0411(2)	†
Si(2)	0·7866(3)	−0·1082(3)	0·1283(2)	†
C(101)	0·9015(17)	0·5308(14)	0·0496(10)	6·5(5)
C(102)	0·6122(15)	0·5379(13)	0·0558(9)	5·0(4)
C(103)	0·7508(16)	0·4065(10)	−0·0647(7)	5·0(3)
C(201)	0·7076(14)	−0·2031(11)	0·1968(8)	5·4(4)
C(202)	0·7533(16)	−0·1511(11)	0·0287(8)	6·2(4)
C(203)	0·9683(15)	−0·1110(12)	0·1488(9)	6·5(4)
C(11)	0·9326(12)	0·3060(10)	0·1312(7)	4·1(3)
O(11)	1·0434(9)	0·3112(8)	0·1325(6)	6·0(3)
C(12)	0·7282(12)	0·4039(10)	0·1978(7)	4·0(3)
O(12)	0·7098(10)	0·4757(8)	0·2384(5)	6·1(3)
C(21)	0·9102(13)	0·1320(11)	0·2586(8)	5·3(3)
O(21)	1·0209(11)	0·1296(9)	0·2580(7)	8·1(3)
C(22)	0·6924(14)	0·2392(11)	0·3178(8)	5·0(4)
O(22)	0·6614(12)	0·3036(9)	0·3608(7)	7·7(4)
C(23)	0·7062(13)	0·0176(10)	0·3205(7)	4·4(3)
O(23)	0·6941(10)	−0·0475(8)	0·3694(6)	6·4(3)
C(1)	0·6904(11)	0·1814(9)	0·0380(7)	3·6(3)
C(2)	0·7601(11)	0·1091(8)	0·0846(6)	2·9(2)
C(3)	0·7159(11)	0·0308(9)	0·1375(6)	3·0(3)
C(4)	0·5890(11)	0·0431(10)	0·1745(7)	3·2(3)
C(5)	0·5311(12)	0·1430(10)	0·1851(7)	3·3(3)
C(6)	0·5413(11)	0·2365(9)	0·1379(7)	3·4(3)
C(7)	0·5836(13)	0·2423(10)	0·0617(8)	3·9(3)

* $B = 8\pi^2U$. † Anisotropic thermal parameters (×10²) in the form: $\exp\{-2\pi^2[U_{11}a^{*2}h^2 + U_{22}b^{*2}k^2 + U_{33}c^{*2}l^2 + 2U_{12}a^*b^*hk + 2U_{13}a^*c^*hl + 2U_{23}b^*c^*kl]\}$.

Atom	U_{11}	U_{22}	U_{33}
Ru(1)	3·88(5)	3·14(5)	2·26(5)
Ru(2)	4·61(6)	3·62(5)	2·36(4)
Si(1)	4·61(19)	2·96(17)	3·37(17)
Si(2)	4·46(19)	2·63(17)	3·10(17)

Atom	U_{12}	U_{13}	U_{23}
Ru(1)	−0·01(4)	0·05(4)	−0·05(3)
Ru(2)	−0·09(4)	0·08(4)	0·17(4)
Si(1)	−0·05(17)	−0·04(19)	−0·67(13)
Si(2)	0·41(14)	0·74(15)	0·40(14)

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* For details of Supplementary Publications see Notice to Authors No. 7 in *J.C.S. Dalton*, 1973, Index issue.

[1] A. Brookes, J. Howard, S. A. R. Knox, V. Riera, F. G. A. Stone, and P. Woodward, *J.C.S. Chem. Comm.*, 1973, 727.

[2] A. Modinos and P. Woodward, *J.C.S. Dalton*, in the press.

[3] Technical Report TR 192, Computer Science Centre, University of Maryland, June 1972.

[4] H. P. Hanson, F. Herman, J. D. Lea, and S. Skillman, *Acta Cryst.*, 1964, **17**, 1040.

TABLE 2

Bond lengths (Å) and angles (°)

(*a*) Distances			
(i) $Ru_2(CO)_5SiMe_3$ group			
Ru(1)–Ru(2)	2·937(1)	C(12)–O(12)	1·156(16)
Ru(1)–Si(1)	2·452(3)	Ru(2)–C(21)	1·914(13)
Si(1)–C(101)	1·839(18)	C(21)–O(21)	1·147(18)
Si(1)–C(102)	1·903(16)	Ru(2)–C(22)	1·906(14)
Si(1)–C(103)	1·923(13)	C(22)–O(22)	1·145(18)
Ru(1)–C(11)	1·876(12)	Ru(2)–C(23)	1·868(13)
C(11)–O(11)	1·150(16)	C(23)–O(23)	1·185(16)
Ru(1)–C(12)	1·855(12)		
(ii) $C_7H_6(SiMe_3)$ ring			
C(1)–C(2)	1·412(16)	Ru(1)–C(2)	2·396(10)
C(2)–C(3)	1·420(15)	Ru(1)–C(1)	2·202(12)
C(3)–C(4)	1·474(16)	Ru(1)–C(7)	2·198(13)
C(4)–C(5)	1·386(17)	Ru(1)–C(6)	2·295(12)
C(5)–C(6)	1·427(17)	Ru(2)–C(2)	2·890(10)
C(6)–C(7)	1·412(18)	Ru(2)–C(3)	2·262(11)
C(7)–C(1)	1·402(18)	Ru(2)–C(4)	2·170(12)
C(3)–Si(2)	1·876(12)	Ru(2)–C(5)	2·310(12)
(*b*) Angles			
Si(1)–Ru(1)–Ru(2)	172·7(1)	Ru(1)–C(12)–O(12)	177·1(11)
Ru(1)–Ru(2)–C(23)	178·1(4)	Ru(2)–C(21)–O(21)	172·5(13)
Ru(1)–Ru(2)–C(21)	87·3(4)	Ru(2)–C(22)–O(22)	174·0(13)
Ru(1)–Ru(2)–C(22)	87·7(4)	Ru(2)–C(23)–O(23)	177·0(11)
C(21)–Ru(2)–C(22)	94·9(6)	C(1)–C(2)–C(3)	130·4(11)
C(21)–Ru(2)–C(23)	94·0(6)	C(2)–C(3)–C(4)	120·4(10)
C(22)–Ru(2)–C(23)	93·4(6)	C(3)–C(4)–C(5)	122·5(11)
Ru(2)–Ru(1)–C(11)	98·1(4)	C(4)–C(5)–C(6)	127·8(11)
Ru(2)–Ru(1)–C(12)	92·9(4)	C(5)–C(6)–C(7)	128·0(11)
C(11)–Ru(1)–C(12)	93·0(6)	C(6)–C(7)–C(1)	120·0(12)
C(11)–Ru(1)–Si(1)	85·5(4)	C(7)–C(1)–C(2)	124·9(11)
C(12)–Ru(1)–Si(1)	80·5(4)	C(2)–C(3)–Si(2)	116·3(8)
Ru(1)–Si(1)–C(101)	114·2(6)	C(4)–C(3)–Si(2)	118·8(8)
Ru(1)–Si(1)–C(102)	111·4(5)	C(3)–Si(2)–C(201)	110·5(6)
Ru(1)–Si(1)–C(103)	114·6(4)	C(3)–Si(2)–C(202)	105·7(6)
C(101)–Si(1)–C(102)	106·5(8)	C(3)–Si(2)–C(203)	112·6(6)
C(101)–Si(1)–C(103)	104·5(7)	C(201)–Si(2)–C(202)	110·2(6)
C(102)–Si(1)–C(103)	104·9(7)	C(201)–Si(2)–C(203)	107·2(7)
Ru(1)–C(11)–O(11)	177·9(11)	C(202)–Si(2)–C(203)	110·7(7)

TABLE 3

Torsion angles (°) around the C_7 ring

C(1)–(2)–(3)–(4)	−24·6	C(5)–(6)–(7)–(1)	−41·5
C(2)–(3)–(4)–(5)	−26·6	C(6)–(7)–(1)–(2)	2·6
C(3)–(4)–(5)–(6)	32·0	C(7)–(1)–(2)–(3)	42·8
C(4)–(5)–(6)–(7)	17·5		

DISCUSSION

The overall configuration of the molecule, and the atom numbering system, are given in Figure 1. The molecule contains an almost linear spine, Si–Ru–Ru–C–O, in addition to which each ruthenium atom carries two carbonyl groups orthogonally related to one another and in an eclipsed configuration with respect to the molecular axis. For this portion of the molecule, therefore, the plane through the two ruthenium atoms bisecting the equatorial carbonyl directions is an approximate mirror plane. The C_7 ring is not symmetrically related to this plane: atoms C(1)—(3) lie on one side of it, and atoms C(4)—(7) on the other (Figure 1). The $SiMe_3$ ring ligand is attached to C(3) with all bonds close to tetrahedral.*

The mode of bonding between the C_7 ring and the two (bonded) ruthenium atoms is best considered from the Ru–C distances. Three of the ring atoms form effectively a π-allyl group, C(3)—(5), directly bonded to Ru(2) at 2·26(1), 2·17(1), and 2·31(1) Å; C(3) is the carbon atom to which the trimethylsilyl group is attached. The other four ring atoms are substantially coplanar and can be considered to form a diene system [C(2)–C(1) and C(6)–C(7)] directly bonded to Ru(1) at 2·40(1), 2·20(1), 2·29(1), and 2·20(1) Å. The Ru(1)–C(2) distance is the longest of these ' bonded ' distances because, although the Ru(2)–C(2) distance must be reckoned, at 2·89(1) Å, as non-bonding, an equality between these two distances would change the formal description of the bonding from ' π-allyl/diene ' to ' π-allyl/bridging C/π-allyl.' Indeed, the latter type of bonding between a C_7H_7 ring and two Ru atoms of a triangular cluster has recently been established for $[Ru_3(CO)_6(C_7H_7)(C_7H_9)]$ [5] and for $[Ru_2I(CO)_4(C_7H_6Ph)]$.[6] The bonding in the title compound could thus be said to veer slightly away from the idealised π-allyl/diene situation towards the more symmetrical one described for $[Ru_3(CO)_6(C_7H_7)(C_7H_9)]$. The C–C distances around the ring are not measured sufficiently accurately to enable individual bond-orders to be evaluated, but suggest extensive delocalisation. The C_7 ring as a whole is distorted to the extent that the angle between the allyl and diene fragments becomes 57°. Torsion angles around the ring are listed in Table 3.

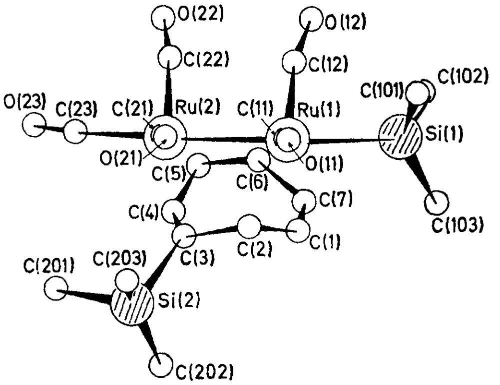

FIGURE 1 The $[Ru_2(CO)_5(SiMe_3)(C_7H_6SiMe_3)]$ molecule, showing the atom numbering system

Along the central O–C–Ru–Ru–Si spine the bond angles (Table 2) show that the sequence is significantly non-linear, most markedly in the case of the $SiMe_3$ group for which Ru–Ru–Si is 173°, and the deviation is away from the C_7 ring. The Ru–Ru distance (2·937 Å) is rather long for a single bond,[7] but on the traditional view of bonding in electronic structures each Ru atom has the residual capacity to react with ligands requiring two orbitals and providing three electrons to Ru(2) and four to Ru(1). This is achieved *via* the C_7 ring in the form of the allyl group to Ru(2) and the diene moiety to Ru(1). In contrast, the Ru(1)–Si(1) bond length (2·452 Å) is rather short for a single bond if the radii of Si and Ru are taken as 1·17 and 1·42 Å, and the Ru–Si–C angles (Table

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* In a preliminary communication on the preparation and structural characterisation of this compound,[1] the Figure inadvertently showed one of the Si–Me bonds pointing backwards instead of forwards.

[5] R. Bau, J. C. Burt, S. A. R. Knox, R. M. Laine, R. P. Phillips, and F. G. A. Stone, *J.C.S. Chem. Comm.*, 1973, 726.

[6] J. A. K. Howard and P. Woodward, unpublished work.

[7] F. A. Cotton and W. T. Edwards, *J. Amer. Chem. Soc.*, 1968, **90**, 5412.

2) of the terminal $SiMe_3$ group are all less than the regular tetrahedral value. In contrast, the $SiMe_3$ ligand which is attached to C(3) of the C_7 ring has bond angles which are all regular.

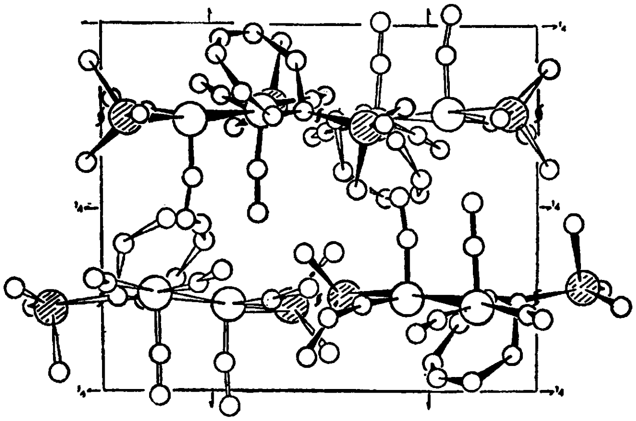

FIGURE 2 One unit cell seen in projection down *c*

The Carbonyl Ligands.—The mean C–O distance for the molecule is $1{\cdot}15_6$ Å and calls for no comment. In many polynuclear carbonyls it is found that axial are significantly shorter than equatorial M–C distances, and that the latter on terminal metal atoms tend to bend towards the centre of the molecule.[8] The asymmetry introduced into the title compound both by the C_7 ring and by the spinal $SiMe_3$ group apparently interferes with both these generalisations, as the axial M–C distance [Ru(2)–C(23) 1·868 Å] is hardly significantly different from the mean equatorial M–C distance (1·888 Å), and whereas the equatorial carbonyl groups on atom Ru(2) do indeed lean towards atom Ru(1) those on Ru(1) in turn lean towards atom Si(1) (see Table 2). The bending of equatorial carbonyl groups towards a terminal silyl group has been observed and discussed for compounds of the type $[R_3SiCo(CO)_4]$.[9]

The overall packing of the molecules in the crystal is illustrated in Figure 2. There are no significantly short intermolecular contacts.

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[4/1334 *Received, 3rd July*, 1974]

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[8] R. Bau, S. W. Kirtley, T. N. Sorrell, and S. Winarko, *J. Amer. Chem. Soc.*, 1974, **96**, 988, and refs. therein.

[9] A. D. Berry, E. R. Corey, A. P. Hagen, A. G. MacDiarmid, F. E. Saalfeld, and B. B. Wayland, *J. Amer. Chem. Soc.*, 1970, **92**, 1940.