Crystal and Molecular Structure of an Unbridged Dinuclear Species with Eclipsed Carbonyl Groups: Bis[tetracarbonyl(trimethylstannio)ruthenium](*Ru-Ru*)

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Crystals of the title compound are triclinic, space group $P\bar{1}$, with $Z = 1$ in a unit cell of dimensions $a = 6.886(1)$, $b = 7.916(2)$, $c = 11.358(2)$ Å, $\alpha = 90.30(2)$, $\beta = 107.73(1)$, $\gamma = 82.93(1)°$. The structure was solved by conventional heavy-atom methods from 1 791 diffracted intensities measured on a diffractometer, and refined to R 0.024. The central chain of the molecule, Sn–Ru–Ru–Sn, is almost linear, and the carbonyl ligands, which lean slightly towards the outer $SnMe_3$ groups, adopt an eclipsed configuration. The Ru–Ru bond [2.943(1) Å] is rather longer than the usual single-bond length, while Ru–Sn bond is correspondingly shorter [2.691(1) Å].

COMPLEXES $[\{Ru(MMe_3)(CO)_4\}_2]$ (M = Si or Ge) have proved to be versatile intermediates both for the synthesis of compounds containing metal–metal bonds, *via* the anions $[Ru(MMe_3)(CO)_4]^-$, and for the preparation of organoruthenium compounds.[1,2] Spectroscopic and other properties suggest that the species $[\{Ru(MMe_3)(CO)_4\}_2]$ are structurally related to decacarbonyl dimanganese in the sense that two halves of the molecule are held together by a metal–metal bond without bridging ligands. It has been assumed [1] that the radial carbonyl ligands in the ruthenium compounds adopt a staggered arrangement. Unfortunately crystals of both the silicon and germanium derivatives $[\{Ru(MMe_3)(CO)_4\}_2]$ proved unsuitable for *X*-ray crystallographic studies, but a suitable single crystal of the tin analogue $[Ru(SnMe_3)(CO)_4]_2$ was obtained.[3] Normally treatment of the anion $[Ru(CO)_4]^{2-}$ with trimethyltin chloride affords $[Ru(SnMe_3)_2(CO)_4]$,[4] but in one synthesis, in which presumably $[Ru_2(CO)_8]^{2-}$ was formed, the title compound was isolated though in exceedingly low yield. Its spectroscopic (i.r., mass, and ^{1}H n.m.r.) properties [3] are very similar to those of the silicon and germanium analogues so that it serves as a useful structural model

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[1] S. A. R. Knox and F. G. A. Stone, *J. Chem. Soc.* (*A*), 1969, 2559; 1971, 2874.

[2] S. A. R. Knox and F. G. A. Stone, *Accounts Chem. Res.*, 1974, **7**, 321.

[3] Julie Edwards, unpublished work.

[4] J. D. Cotton, S. A. R. Knox, and F. G. A. Stone, *J. Chem. Soc.* (*A*), 1968, 2758.

for this family of compounds. Moreover, there has recently been considerable interest[5] in staggered *vs.* eclipsed radial carbonyl ligands in binuclear metal carbonyls. These considerations prompted us to undertake the work herein described.

EXPERIMENTAL

Crystals of $[\{Ru(SnMe_3)(CO)_4\}_2]$ were yellow prisms. A crystal $0.16 \times 0.09 \times 0.13$ mm was mounted on a Syntex $P2_1$ four-circle diffractometer and intensities collected for $3.7° < 2\theta < 50.0°$ according to methods described earlier.[6] Of the total 2 139 reflections, 1 921 having $I > 2.5\sigma(I)$ were deemed observed.

RESULTS

Crystal Data.—$C_{14}H_{18}O_8Ru_2Sn_2$, $M = 753.8$, Triclinic, $a = 6.886(1)$, $b = 7.916(2)$, $c = 11.358(2)$ Å, $\alpha = 90.30(2)$, $\beta = 107.73(1)$, $\gamma = 82.93(1)°$. $U = 584.9$ Å^3, $D_m = 2.09$, $Z = 1$, $D_c = 2.15$ g cm^{-1}, $F(000) = 1\,416$. Space group $P\bar{1}$. Mo-K_α *X*-radiation (graphite monochromator), $\lambda = 0.710\,69$ Å; μ(Mo-K_α) = 34.0 cm^{-1}.

TABLE 1

Atomic positional and thermal ($\times 10^2$) parameters,* with estimated standard deviations in parentheses

Atom	x/a	y/b	z/c	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ru	0.08172(6)	0.10218(5)	0.10834(3)	3.73(2)	3.46(2)	3.77(2)	−0.84(2)	1.22(2)	−0.51(2)
Sn	0.21008(6)	0.29192(5)	0.30776(3)	4.83(2)	4.90(2)	4.41(2)	−1.27(2)	1.50(2)	−1.40(2)
C(1)	0.2896(9)	0.1730(6)	0.0421(5)	5.0(3)	4.3(3)	4.8(3)	−0.4(3)	1.7(3)	−0.1(2)
O(1)	0.4155(6)	0.2139(5)	0.0085(4)	6.1(3)	6.9(3)	8.5(3)	−1.7(2)	3.8(2)	0.1(2)
C(2)	0.2785(9)	−0.0855(7)	0.1961(5)	4.9(3)	4.7(3)	5.5(3)	−1.2(3)	1.0(3)	−0.1(3)
O(2)	0.3943(7)	−0.1944(5)	0.2507(4)	6.9(3)	6.4(3)	8.8(3)	−0.0(2)	−0.1(3)	1.9(2)
C(3)	−0.1190(9)	0.0326(7)	0.1801(5)	4.9(3)	5.0(3)	4.6(3)	−1.2(3)	1.5(3)	−0.6(2)
O(3)	−0.2293(7)	−0.0094(6)	0.2268(4)	6.9(3)	8.5(3)	7.6(3)	−1.9(3)	4.1(3)	−0.2(2)
C(4)	−0.1110(9)	0.2980(7)	0.0270(5)	5.1(3)	4.1(3)	5.4(3)	−1.3(3)	1.8(3)	−0.4(3)
O(4)	−0.2186(7)	0.4149(5)	−0.0188(4)	7.0(3)	4.8(2)	9.1(3)	0.6(2)	0.9(3)	1.1(2)
C(11)	0.5211(10)	0.3465(9)	0.3427(6)	5.3(4)	10.0(5)	8.3(5)	−2.2(4)	1.3(4)	−3.7(4)
C(12)	0.1969(12)	0.1598(9)	0.4690(6)	10.5(6)	10.4(6)	4.8(4)	−2.6(5)	1.4(4)	−0.0(4)
C(13)	0.0226(10)	0.5320(8)	0.2962(6)	7.5(5)	6.3(4)	9.7(5)	−0.6(4)	3.6(4)	−2.9(4)
H(111) †	0.567	0.414	0.409						
H(112)	0.611	0.243	0.350						
H(113)	0.528	0.408	0.268						
H(121)	0.062	0.141	0.460						
H(122)	0.286	0.055	0.482						
H(123)	0.244	0.228	0.541						
H(131)	0.068	0.600	0.364						
H(132)	0.026	0.594	0.223						
H(133)	−0.113	0.513	0.284						

* Anisotropic thermal parameters in the form: $\exp - 2\pi^2[U_{11}a^{*2}h^2 + U_{22}b^{*2}k^2 + U_{33}c^{*2}l^2 + 2U_{12}a^*b^*hk + 2U_{13}a^*c^*hl + 2U_{23}b^*c^*kl]$. † Isotropic thermal parameters in the form $B = 8\pi^2U$, set at $U = 0.088$.

Structure Solution and Refinement.—In view of the fact that the triclinic unit cell contains only one molecule, it was considered best to assume space-group symmetry $P1$ and not $P\bar{1}$; the latter would necessarily imply a centre of symmetry in the molecule and hence an eclipsed arrangement of carbonyl ligands. The metal atoms were located from a Patterson synthesis, and the remaining atoms from successive electron-density difference syntheses. The overall arrangement is in fact centrosymmetric. Refinement of the structure therefore subsequently assumed space group $P\bar{1}$ with half a molecule as the crystallographic asymmetric unit. Convergence was obtained at R 0.024 (R' 0.026) with anisotropic thermal parameters for all non-hydrogen atoms- hydrogen atoms were included at fixed positional parameters with U fixed at 0.088. Weights were applied according to $1/w = \sigma_F^2$ and a satisfactory weight analysis obtained. In the final least-squares refinement cycle the mean shift-to-error ratio was 0.01 and a last electron-density difference synthesis showed no peaks > 0.4 or < -0.4 eÅ^{-3}. Atomic scattering factors for non-hydrogen atoms were those of ref. 7 and for hydrogen those of ref. 8. All computational work (including an absorption connection) was carried out on a CDC 7600 of the University of London with the '*X*-Ray' system of programs.[9] Observed and calculated structure factors are listed in Supplementary Publication No. SUP 21 449 (16 pp., 1 microfiche).* Final atomic and thermal parameters are listed in Table 1.

DISCUSSION

The overall configuration of the molecule is shown in Figure 1, which also includes the atom numbering sequence. Our results establish that the $[\{Ru(SnMe_3)(CO)_4\}_2]$ molecule comprises the atom sequence Sn–Ru–Ru–Sn, with four equatorial CO groups on each Ru atom in an eclipsed configuration.

Figure 2 shows diagrammatically the relationship of the equatorial carbonyl groups to one another and to the terminal Sn–C bonds; also the relationship between adjacent molecules. Because $Z = 1$, the packing is such that all carbonyl groups are either mutually parallel or perpendicular. The idealised overall molecular symmetry is $2/m$ (C_{2h}); in Figure 2 the two-fold axis horizontal in the plane of the paper, with the mirror plane perpendicular to it.

Along the central spine of the molecule the bond

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* For details see Notice to Authors No. 7 in *J.C.S. Dalton*, 1974, Index issue.

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

[6] A. Modinos and P. Woodward, *J.C.S. Dalton*, 1974, 2065.

[7] D. T. Cromer and J. B. Mann, *Acta Cryst.*, 1968, **A24**, 321.

[8] R. F. Stewart, E. R. Davidson, and W. Simpson, *J. Chem. Phys.*, 1968, **42**, 3175.

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

angles (Table 2) show that the Sn–Ru–Ru–Sn sequence is slightly, but significantly, non-linear, presumably because the three-fold symmetry of the $SnMe_3$ group cannot be superimposed upon the four-fold symmetry of the $Ru(CO)_4$ entity in such a way as to make all Me–CO relationships equivalent. The Ru–Ru bond is rather long[10] for a single bond [2.943(1) Å]; any suggestion that the eclipsed configuration adopted by the carbonyl ligands might be accounted for by multiple bonding can certainly be dismissed. Indeed, the eighteen electron rule predicts that each ruthenium atom has a closed shell if a two-centre electron-pair ruthenium–ruthenium bond is assumed. A list of Ru–Ru bond lengths abstracted from structure determinations on a series of polynuclear organometallic compounds has been deposited with the structure-factor Table. The Ru–Sn bond, in contrast, is rather short [2.691(1) Å] if the radii of Ru and Sn are taken as 1.42 and 1.40 Å. Moreover, the C–Sn–C angles of the terminal $SnMe_3$ groups are all less than the ideal tetrahedral value, giving more *p* character to the Sn–C bonds and more *s* character to the Ru–Sn bond. We have already reported[11] a parallel situation for silyl ligands in the molecule $[Ru_2(CO)_5(SiMe_3)(C_7H_6SiMe_3)]$. The mean Sn–C distance (2.14_7 Å), is not significantly different from the sum of the sp^3 covalent radii.

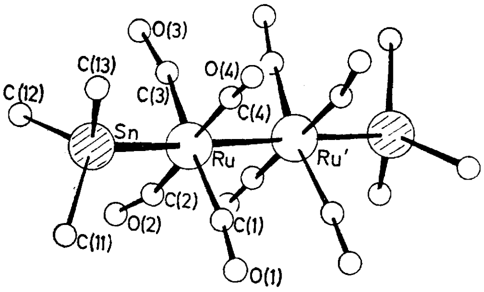

FIGURE 1 Overall configuration of the molecule, showing the atom-numbering sequence

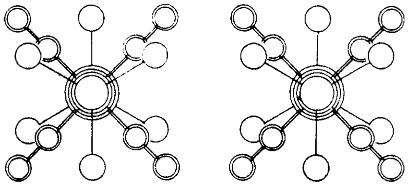

FIGURE 2 View along the molecular axis, showing the relationship of one molecule to its neighbour in the crystal

TABLE 2

Bond lengths (Å) and angles (°)

(*a*) Distances			
Ru–Ru′	2.943(1)	C(2)–O(2)	1.140(6)
Ru–Sn	2.691(1)	C(3)–O(3)	1.130(9)
Ru–C(1)	1.947(7)	C(4)–O(4)	1.130(6)
Ru–C(2)	1.932(5)	Sn–C(11)	2.154(7)
Ru–C(3)	1.938(7)	Sn–C(12)	2.145(7)
Ru–C(4)	1.944(5)	Sn–C(13)	2.143(6)
C(1)–O(1)	1.129(8)		
(*b*) Angles			
Ru′–Ru–Sn	176.8(3)	Sn–Ru–C(3)	87.6(2)
Ru′–Ru–C(1)	92.1(2)	Sn–Ru–C(4)	88.5(2)
Ru′–Ru–C(2)	92.9(2)	Ru–C(1)–O(1)	177.2(5)
Ru′–Ru–C(3)	89.6(2)	Ru–C(2)–O(2)	178.1(7)
Ru′–Ru–C(4)	89.9(2)	Ru–C(3)–O(3)	176.9(5)
C(1)–Ru–C(2)	89.2(2)	Ru–C(4)–O(4)	177.9(7)
C(1)–Ru–C(3)	177.8(2)	Ru–Sn–C(11)	113.3(2)
C(2)–Ru–C(3)	89.8(2)	Ru–Sn–C(12)	109.6(2)
C(2)–Ru–C(4)	177.1(2)	Ru–Sn–C(13)	113.4(2)
C(3)–Ru–C(4)	90.2(2)	C(11)–Sn–C(12)	107.4(3)
C(4)–Ru–C(1)	90.7(2)	C(12)–Sn–C(13)	106.0(3)
Sn–Ru–C(1)	90.6(2)	C(13)–Sn–C(11)	106.7(3)
Sn–Ru–C(2)	88.7(2)		

The Carbonyl Ligands.—The mean C–O distance is 1.13_3 and the mean Ru–C distance 1.94_0 Å; both are within the ranges commonly observed. The most remarkable feature of the molecule, however, is the fact that the carbonyl groups on the two Ru atoms adopt an eclipsed configuration. Arguments relating to eclipsed *vs.* staggered arrangements of carbonyl groups in linear polynuclear carbonyls have been fully presented[5] and need not be rehearsed here, but it is evident that the energy of interconversion of the two forms must be of the same order as that of the crystal-packing forces, and the possibility obviously exists that the very neat packing of the molecules in the eclipsed configuration is, in the case of the title compound, the over-riding factor. In any case, interactions between the antibonding orbitals of the carbonyl groups on one ruthenium atom and the *d* orbitals of the other metal atom, sometimes believed to constrain equatorial carbonyl groups into a staggered configuration,[5] are likely to be of especially little significance here because of the unusually long Ru–Ru bond and because of the bending of the carbonyl groups away from the molecular centre (see later). It would be especially interesting to know the configuration of the $[\{Ru(SnMe_3)_2(CO)_4\}_2]$ molecule in solution.

Another feature commonly found in polynuclear carbonyls is that equatorial groups on terminal metal atoms tend to bend towards the centre of the molecule[5] except in so far as any interactions with the terminal axial group may determine otherwise. However, it has been shown that a terminal R_3Si group in compounds $[Co(SiR_3)(CO)_4]$ causes the equatorial carbonyl groups to bend towards the silyl group.[12] The title compound shows a small, but significant, deviation of the latter kind (mean Sn–Ru–C 88.8°). The Ru–C–O bonds are almost linear, though the deviations appear to be just significant on the errors given.

We thank the S.R.C. for financial support, and Miss Julie Edwards for crystals.

[5/539 *Received*, 19*th March*, 1975]

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