Crystal Structure of Di-μ-(dimethylsilylene)-bis[tricarbonyl(trimethylsilyl)ruthenium(III)] and a Re-evaluation of the Metal–Metal Interaction in Tri-μ-chloro-diruthenium Complexes

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The molecular structure of the title compound has been determined by single-crystal *X*-ray diffraction analysis from diffractometer data. The structure was solved by Patterson and Fourier methods and refined by least squares to *R* 0·060 for 658 independent reflections. Crystals are monoclinic, space group $P2_1/c$, $a = 10{\cdot}64$, $b = 9{\cdot}34$, $c = 14{\cdot}00$, $\beta = 109°$, $Z = 2$. The molecule, which is similar to its tin analogue, contains a Ru–Ru bond of 2·96 Å. The relevance of this result to metal–metal bonding in tri-μ-chloro-diruthenium complexes is discussed.

METALLIC bonding has been of considerable interest to inorganic chemists for years, but the evidence for such interactions in organometallic complexes is not always straightforward and can be misinterpreted, particularly when dealing with interatomic distances from *X*-ray structural studies. For example, *X*-ray analysis[1] of $Ru_2Cl_5(PBu^n{}_3)_4$ gave the Ru–Ru distance as 3·115 Å, which was interpreted as a non-bonding distance, although in the analysis[2] of $[(Me_3Sn)(CO)_3Ru(SnMe_2)]_2$ [compound (II)], evidence was presented for the existence of a strong attractive interaction between the ruthenium atoms at 3·116 Å. In both compounds the central metal atoms form six metal–ligand σ-bonds oriented approximately octahedrally, and although the number of bridging and terminal groups differ, it is surprising that the same Ru–Ru distance should be interpreted in two entirely different ways in these two compounds.

In order to corroborate the existence of extensive overlap between ruthenium atom orbitals at 3·12 Å, and thus clarify the bonding situation in these diruthenium complexes, the *X*-ray crystal structure analysis of $[(Me_3Si)(CO)_3Ru(SiMe_2)]_2$ [compound (I)] was undertaken. The existence of extensive overlap would be proven if a Ru–Ru distance $<3{\cdot}12$ Å resulted when the large bridging tin atoms in (II) were replaced by smaller silicon atoms. This result was predicted[2] and has now been observed.

EXPERIMENTAL

Golden yellow plate-like crystals were prepared by the method of ref. 3. A single diamond-shaped crystal, of dimensions *ca.* 0·05 × 0·3 × 0·3 mm, was mounted along the crystallographic *c* axis, which coincides with the long diagonal in the plate face (the [100] direction corresponds to the plate normal).

Although crystals exposed to moist air decomposed and turned black slowly over a period of months, the crystal selected for data collection was well protected by the mounting medium and showed little tendency to deteriorate, as determined by direct observation and by continuous monitoring of standard intensities.

The space group and approximate unit-cell parameters were determined from Weissenberg and precession photographs, and accurate lattice constants were derived from a least-squares refinement of 40 reflections which were well centred on the diffractometer. Intensity data were collected in the θ—2θ scan mode between sin θ/λ values of 0·0985 and 0·4105 with zirconium-filtered Mo-K_α radiation on an Enraf-Nonius PAD 3 diffractometer. Of the 808 intensities measured from the *hkl* and $\bar{h}kl$ octants, 658 independent reflections were used in the subsequent refinement and had $I > 2\sigma(I)$ where $\sigma^2(I) = C_s + (t_s/2t_b)^2(C_{B1} + C_{B2})$, C_s is the total number of counts collected during the scan time t_s, and C_{B1} and C_{B2} are the stationary background counts on both sides of the peak, each measured during time t_b.

Crystal Data.—$C_{16}H_{30}O_6Ru_2Si_4$, $M = 632{\cdot}89$, Monoclinic, $a = 10{\cdot}64(1)$,† $b = 9{\cdot}341(5)$, $c = 14{\cdot}00(2)$, $\beta = 109{\cdot}4(2)°$, $U = 1391$ Å^3, $Z = 2$, $D_c = 1{\cdot}23$,‡ $F(000) = 636$. Space group $P2_1/c$. Mo-K_α radiation $\lambda = 0{\cdot}7107$ Å; μ(Mo-K_α) = 12·5 cm^{-1}.

Lorentz and polarization corrections were applied to yield observed structure amplitudes, but no absorption, extinction, or dispersion corrections were applied. Structure factor calculations were carried out by use of the atomic scattering factors of ref. 4.

The structure was solved § using standard Patterson and Fourier techniques, and several block-diagonal least-squares cycles with unit weights and isotropic thermal motion reduced *R* to 0·079. A difference-Fourier synthesis revealed no significant features except those related to the thermal anisotropy of the Ru atom. Further full-matrix weighted least-squares refinement of a model containing anisotropic thermal motion for Ru and isotropic motion for all other atoms reduced *R* to 0·060 and *R'* (the weighted favtor) to a final value of 0·050. Table 1 lists the atomic and thermal parameters of all fourteen non-hydrogen atoms in the crystallographically independent unit. Table 2 lists relevant angles and intramolecular distances. Final calculated and observed structure amplitudes are listed in Supplementary Publications No. SUP 20512 (5 pp., 1 microfiche). ¶

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† Throughout this paper, estimated standard deviations for the last significant figure are in parentheses.

‡ D_m was not measured owing to lack of material.

§ All programs used in the solution of the structure were part of the crystallographic computing system '*X*-Ray '67,' J. I. Stewart, University of Maryland Technical Report TR 67 58. Data collection and reduction programs were written for the Enraf-Nonius Diffractometer by S. F. Watkins.

¶ For details see Notice to Authors No. 7 in *J. Chem. Soc.* (*A*), 1970, Issue No. 20 (items less than 10 pp. are sent as full size copies).

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TABLE 1

Fractional atomic co-ordinates and temperature factor components (Å^2)

	X	*Y*	*Z*	*B*
Ru	0·0863(2)	0·1247(2)	0·0014(1)	*
Si(1)	0·3175(6)	0·2259(8)	0·0667(5)	4·9(2)
Si(2)	0·1574(6)	−0·0965(8)	0·0886(4)	3·8(2)
C(1)	0·142(2)	0·045(2)	−0·102(2)	4·8(6)
C(2)	0·070(2)	0·192(2)	0·123(2)	3·7(6)
C(3)	0·035(2)	0·301(3)	−0·062(1)	3·7(6)
O(1)	0·182(1)	−0·008(2)	−0·161(1)	5·6(4)
O(2)	0·060(1)	0·228(2)	0·199(1)	5·9(4)
O(3)	0·013(1)	0·416(2)	−0·100(1)	5·5(4)
C(4)	0·265(2)	−0·231(2)	0·047(1)	4·5(5)
C(5)	0·213(2)	−0·112(3)	0·234(1)	4·9(5)
C(6)	0·459(2)	0·103(3)	0·125(2)	8·8(7)
C(7)	0·336(2)	0·368(3)	0·166(2)	8·2(7)
C(8)	0·362(2)	0·317(2)	−0·040(2)	5·8(6)

* Components of the thermal ellipsoid tensor *B* (Å^2) in the form $T = \exp(\frac{1}{4}r\cdot B\cdot r)$, where $r = ha^* + kb^* + lc^*$

	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Ru	4·19(12)	3·18(10)	3·63(07)	0·08(11)	1·52(06)	−0·15(15)

TABLE 2

Intramolecular bond lengths (Å) and bond angles (°)

(*a*) Distances

Ru–Ru′	2·958(3)	C(2)–O(2)	1·16(3)
Ru–Si(1)	2·507(8)	C(3)–O(3)	1·19(3)
Ru–Si(2)	2·391(7)	Si(1)–C(6)	1·85(3)
Ru–Si(2′)	2·491(8)	Si(1)–C(7)	1·88(3)
Ru–C(1)	1·89(3)	Si(1)–C(8)	1·91(3)
Ru–C(2)	1·88(2)	Si(2)–C(4)	1·92(2)
Ru–C(3)	1·86(2)	Si(2)–C(5)	1·93(2)
C(1)–O(1)	1·16(3)		

(*b*) Angles

Si(2)–Ru–Si(2′)	105·4(2)	Ru–C(1)–O(1)	176(2)
C(1)–Ru–Si(2)	85·8(7)	Ru–C(2)–O(2)	177(2)
C(1)–Ru–Si(2′)	96·3(6)	Ru–C(3)–O(3)	175(2)
C(1)–Ru–C(3)	96(1)	C(7)–Si(1)–C(8)	106(1)
C(1)–Ru–Si(1)	84·6(6)	C(6)–Si(1)–C(7)	104(1)
C(2)–Ru–Si(2)	86·4(6)	C(6)–Si(1)–C(8)	104(1)
C(2)–Ru–Si(2′)	95·7(6)	Ru–Si(1)–C(6)	118·8(9)
C(2)–Ru–C(3)	91·9(9)	Ru–Si(1)–C(7)	112·6(8)
C(2)–Ru–Si(1)	85·3(6)	Ru–Si(1)–C(8)	110·7(6)
C(2)–Ru–C(1)	167·0(8)	C(4)–Si(2)–C(5)	105·5(9)
C(3)–Ru–Si(2)	177·7(6)	Ru–Si(2)–C(4)	122·1(7)
C(3)–Ru–Si(2′)	76·2(6)	Ru–Si(2)–C(5)	122·5(8)
C(3)–Ru–Si(1)	86·4(6)	Ru′–Si(2)–C(4)	113·7(6)
Si(2)–Ru–Si(1)	92·0(2)	Ru′–Si(2)–C(5)	115·5(7)
Si(2′)–Ru–Si(1)	162·6(2)		

DISCUSSION

The molecular structure of (I) is similar to that of (II);[2] in both, monomeric units based on octahedral co-ordination polyhedra share an edge to form the dimer. The central Ru atom of each monomer unit is bonded to three terminal carbonyls (one equatorial and two axial with reference to the Ru_2Si_2 bridge plane), one terminal trimethylsilyl group, and two bridging dimethylsilylene groups (Figures 1 and 2). The Ru_2Si_2 bridge plane contains the crystallographic centre of symmetry and the site-symmetry is thus C_i, although the molecular symmetry deviates only slightly from C_{2h}.

Existence of a strong Ru–Ru bond in the Ru_2Si_2 bridge plane is deduced, as it was in (II), by the observed distortions in the bridge bond angles. These distortions have been discussed elsewhere,[2] when it was argued that the Ru–Ru bond had been stretched to 3·12 Å owing to the size of the bridging tin atoms. That argument is amply supported by the present structure in which the Ru–Ru distance is 2·96 Å, a decrease due to the replacement of tin by smaller silicon atoms in the bridge. Comparable Ru–Ru distances have recently been found in $Ru_3(CO)_9H(PhCC_6H_4)$ (2·91 Å),[5] $H_3Ru_3(CO)_9(C_{12}H_{15})$ (2·92 Å),[6] and $[(Me_2Ge)Ru(CO)_3]_3$ (2·93 Å).[7]

If the co-ordinate system on each central Ru^{III} is defined such that the *x* and *y* axes lie approximately along the Ru–Si bridge bonds, then each metal uses d^2sp^3 hybrid orbitals to form six σ-bonds to the silicon and carbon atoms. Two metal d_{xy} orbitals then overlap directly in the bridge plane to form a metal–metal σ-bond, into which two of the ten metal electrons are placed.

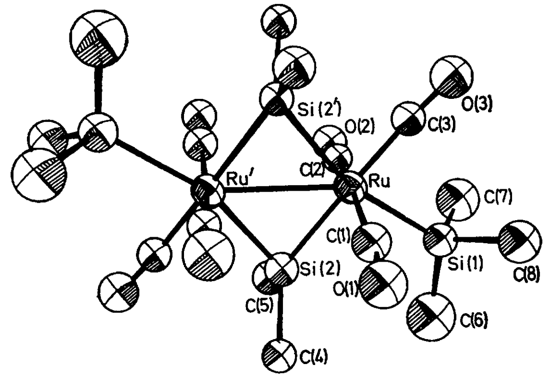

FIGURE 1 Molecular structure of $[(Me_3Si)(CO)_3Ru(SiMe_2)]_2$, showing the numbering system used

While the major distortions in $[(Me_3Sn)Ru(CO)_3(SnMe_2)]_2$ and $[(Me_3Si)Ru(CO)_3(SiMe_2)]_2$ are due to the metal–metal bond, interesting trends are evident in other bond lengths in these two molecules. For example, in (I) the two Ru–Sn bonds mutually *trans* are of equal length and close to the value estimated for a single bond, but the third Ru–Sn bond, which is *trans* to a carbonyl, is significantly shorter. This trend persists when Si is substituted for Sn. The two mutually *trans* Ru–Si bonds, Ru–Si(1) and Ru–Si(2′), are of equal length to within 2σ, mean 2·50(1) Å. The bond length between Ru and Si(2) is significantly shorter than this, 2·402(7) Å. The estimated Ru–Si single-bond length is 2·44 Å.[8] These bond length data may indicate that the Me_3M^{IV} and Me_2M^{IV} (M^{IV} = Si, Sn, and probably Ge) ligands have a greater *trans*-influence than CO. Chatt and his co-workers[9] and Glockling and Hooton[10] have observed the large inductive *trans*-effect of substituted silyl and germyl groups in platinum compounds, and Mason and

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[9] J. Chatt, C. Eaborn, S. D. Ibekwe, and P. N. Kapoor, *J. Chem. Soc.* (*A*), 1970, 1343.

[10] F. Glockling and K. A. Hooton, *J. Chem. Soc.* (*A*), 1967, 1066.

Towl[11] have discussed the factors involved in the *trans*-influence in octahedral complexes.

The extent to which any of the Ru–Si bonds differ from ' single ' bonds is difficult to ascertain, although clearly all three are not of exactly the same bond order. There has been much discussion of the possibility of d_π–d_π bonding between transition metals and Group IV elements,[12–15] and certainly the possibility exists in $[(Me_3Si)Ru(CO)_3(SiMe_2)]_2$ of overlap between empty $3d$ orbitals on silicon with the filled $4d_{xz}$ and $4d_{yz}$ orbitals of ruthenium. A similar interaction was postulated for $[(Me_3Sn)Ru(CO)_3(SnMe_2)]_2$.[2]

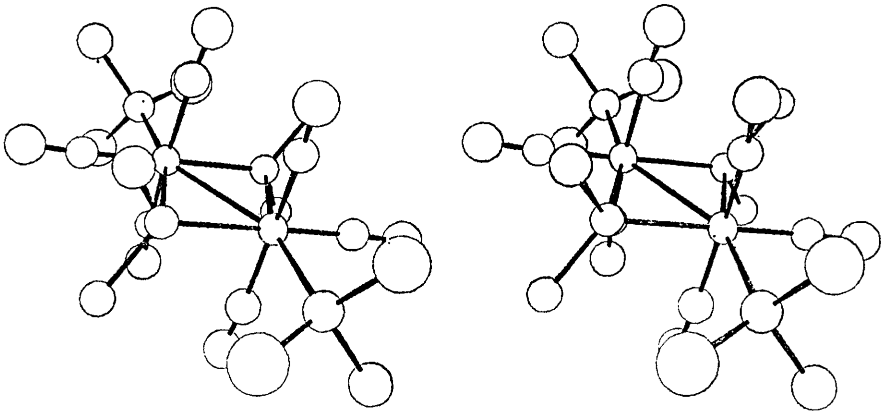

FIGURE 2 Stereopair drawing of $[(Me_3Si)(CO)_3Ru(SiMe_2)]_2$

An interesting effect, first suggested by MacDiarmid[14] and which is small but observable and consistent in both (I) and (II), is the interaction between the axial carbonyls and the short Ru–M^{IV} bond. Ru–C(1) and Ru–C(2) are not exactly perpendicular to the bridge plane, but are tilted from the perpendicular toward the closest M^{IV} atom (7° for M^{IV} = Si, 4° for M^{IV} = Sn). In neither compound are there any inter- or intra-molecular contact distances short enough to cause this bending and we conclude that a weak three-centre interaction may exist between Ru $4d_{yz}$, Si $3d$ or Sn $5d$, and CO $2p_{\pi^*}$ orbitals. A similar interaction is found in $[Fe(CO)_4(GeEt_2)]_2$,[16] except that the axial carbonyls are tilted to interact with all Fe–Ge bridge bonds equally. The sums of van der Waal's radii for M^{IV} and a carbonyl carbon have been given,[14] but in all the three molecules already discussed the CO–M^{IV} distance is at least 0·2 Å less than these values, thereby reinforcing the possibility of an electronic interaction.

We now examine qualitatively the metal–metal interaction in tri-μ-chloro-diruthenium complexes $L_6Ru_2Cl_3$. Initially all interactions with the terminal ligands L may be ignored, for we shall be interested in the behaviour of those electrons which do not take part in the Ru–Cl and Ru–L σ-bonding system. The local symmetry at the metal in each $L_3RuCl_{3/2}$ moiety is approximately C_{3v}, and three orbitals which do not participate in the framework σ-system, d_{xy}, d_{yz}, and d_{xz}, form bases for irreducible representations A_1 and E. In other words, hybrid atomic orbitals, of functional form $\psi(A_1) = \frac{1}{\sqrt{3}}(d_{xy} + d_{yz} + d_{xz})$, $\psi_1(E) = \frac{1}{\sqrt{2}}(d_{xy} - d_{yz})$, and $\psi_2(E) = \frac{1}{\sqrt{6}}(2d_{xz} - d_{xy} - d_{yz})$, may be formed on each metal atom. The $\psi(A_1)$ orbital is maximum along the Ru–Ru internuclear line, and overlap between the two A_1 orbitals results in a strong metal–metal bonding orbital and a metal–metal antibonding orbital. The $\psi(E)$ orbitals are not maximum along the internuclear line, and it is expected that overlap between them will not be as great as between the A_1 orbitals. A suggested MO diagram is shown in Figure 3, with six MO's forming the Ru_2 bonding system. These orbitals also form equivalent bases for irreducible representations in D_{3h}.

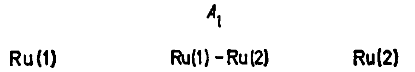

FIGURE 3 Schematic representation of metal bonding orbitals in tri-μ-chloro-diruthenium complexes

The foregoing discussion applies to molecules of the type $[Ru_2Cl_3A_nL_{6-n}]^m$ where A is an anionic terminal ligand, L is a neutral terminal ligand, and m is the charge. The two metal atoms contain $(16 - 3 - n - m)$ elec-

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trons which do not contribute to σ-bonding, and which therefore reside in metal MO's. $[Ru_2Cl_3(PEt_2Ph)_6]^+$ and $Ru_2Cl_4(PEt_2Ph)_5$ each contain twelve electrons which completely fill the A_1 and E metal MO's. The resulting Ru–Ru bond order of zero correlates with the observed distances of 3·44 [17] and 3·37 Å.[18] In paramagnetic $Ru_2Cl_5(PBu^n_3)_4$ the eleven electrons fail to fill all six metal MO's, and the observed [1] 3·12 Å distance corresponds to a Ru–Ru bond order of *ca.* 0·5 (the same distance in $[(Me_3Sn)(CO)_3Ru(SnMe_2)]_2$ corresponds to a full single-bond which has been stretched). Further, the paramagnetic electron in the delocalized metal antibonding orbital is shared equally between the metals, hence no difference was observed between the two ruthenium atoms.

Although little or no orbital interaction between the terminal ligands and the metal orbitals is expected for the three compounds, the same is not true for $(SnCl_3)$-$Ru_2Cl_3(CO)_5$. Twelve electrons from the two metals must reside in molecular orbitals which contain substantial contributions from the terminal ligand π-systems. Qualitatively, the effect is to withdraw electron density from the metal–metal antibonding orbitals into terminal ligand π-orbitals, thus increasing the Ru–Ru bond order from zero. This is consistent with the observed [19] distance of 3·157 Å.

Finally, this simple bonding picture could be extended to include β-$RuCl_3$, which contains [20] $RuCl_3$ fragments of C_{3v} symmetry linked by trichloro-bridges in infinite chains. Each metal contributes five electrons, or ten per Ru_2 pair, so the observed Ru–Ru distance of 2·83 Å corresponds to a bond of order 1·0, not unlike the Ru–Ru bond of 2·85 Å in $Ru_3(CO)_{12}$.[21] However, the bonding and physical properties of β-$RuCl_3$ are complicated by the formation of delocalized bands down the infinite chain, and a more extensive theoretical treatment would be needed to describe this substance adequately.

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