Crystal Structures of Two Diruthenium Carbonyl Complexes derived from Cyclo-octatetraene, $[Ru_2(C_8H_8SiMe_2CH_2CH_2SiMe_2)(CO)_5]$ and $[Ru_2(C_8H_8SiMe_3)(SiMe_3)(CO)_4]$ †

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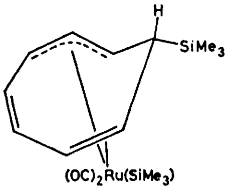
Cyclo-octatetraene reacts with the complex $[Ru(SiMe_2CH_2CH_2SiMe_2)(CO)_4]$ to give, as one product, the species $[Ru_2(C_8H_8SiMe_2CH_2CH_2SiMe_2)(CO)_5]$ (5). An *X*-ray diffraction study shows that the bonding between the C_8 ring and the two ruthenium atoms is of a novel symmetrical kind comprising a central interannular π-allyl moiety and two ethylenic bonds. The carbonyl ligands are symmetrically related to the mirror plane of the C_8 ring [structure (5) in text]. Crystals of (5) are triclinic, with $Z = 2$ in a unit cell with dimensions $a = 11.851(2)$, $b = 8.761(2)$, $c = 11.864(2)$ Å, $\alpha = 100.54(2)$, $\beta = 110.37(1)$, $\gamma = 92.25(1)°$, and space group $P\bar{1}$. The structure has been solved by heavy atom methods from 4 347 intensities $[I > 1.75\sigma(I)]$ measured on a four-circle diffractometer and refined to R 0.046. The complex $[Ru_2(C_8H_8SiMe_3)(SiMe_3)(CO)_4]$ (7) is formed by thermolysis of $[Ru_2(C_8H_8SiMe_3)(SiMe_3)(CO)_5]$ (6), a high-yield product of treating $[Ru(C_8H_8SiMe_3)(SiMe_3)(CO)_2]$ with $[Ru_3(CO)_{12}]$, and which is believed, on spectroscopic grounds, to have a structure closely similar to that of (5) as far as the mode of attachment of the ring to the metal carbonyl spine is concerned. An *X*-ray study of (7) shows that a novel ring-opening reaction has occurred; although the spinal sequence $Me_3SiRu(CO)_2Ru(CO)_2$ of the precursor is retained, the two $Ru(CO)_2$ units are now twisted relative to one another and the C_8 ring has opened to form a contorted chain, σ-bonded to one Ru atom at one end and to the terminal $SiMe_3$ group at the other [structure (7) in text]. Crystals of (7) are triclinic, with $Z = 2$ in a unit cell with dimensions $a = 6.903(3)$, $b = 7.669(3)$, $c = 24.454(10)$ Å, $\alpha = 92.41(3)$, $\beta = 89.87(3)$, $\gamma = 116.45(3)°$, and space group $P\bar{1}$. The structure has been solved by heavy-atom methods from 3 485 intensities $[I > 1.75\sigma(I)]$, and refined to R 0.055.

CYCLO-OCTATETRAENE is known[1] to react with $[Ru(SiMe_3)_2(CO)_4]$ (1) in hexane under reflux to give initially compounds of type (2) in which a trimethylsilyl group has migrated to the hydrocarbon ligand. Under more vigorous conditions (heptane and octane under reflux) these same reactions yield diruthenium complexes of pentalene (3) directly, strongly suggesting that (2) undergoes thermolysis to yield (3). The crystal structure of the trimethylgermyl analogue of (3) has been determined.[2] In an extension of studies on the migration of trimethylsilyl groups from metal to co-ordinated hydrocarbon, the reaction between cyclo-octatetraene and complex (4) was studied.[3,4] Among the products was one of chemical composition $[Ru_2(C_8H_8SiMe_2CH_2CH_2SiMe_2)(CO)_5]$ (5). The molecular structure of (5) has now been established from a single-crystal *X*-ray diffraction study which forms part of the subject of this paper; it indicates, among other features, ring-to-metal bonding of a new type. Furthermore, from the reaction of $[Ru(C_8H_8SiMe_3)(SiMe_3)(CO)_2]$ (2) with $[Ru_3(CO)_{12}]$ or with (1) a product of molecular formula $[Ru_2(C_8H_8SiMe_3)(SiMe_3)(CO)_5]$ was obtained in good yield.[5] This has spectroscopic properties which are almost identical to those of (5), strongly suggesting that the ring-to-metal bonding is the same in both and therefore implying structure (6). When this complex (6) is heated in octane, carbon monoxide is released and an almost quantitative conversion into $[Ru_2(C_8H_8SiMe_3)(SiMe_3)(CO)_4]$ takes place. The ^{13}C n.m.r. spectrum of this complex suggests that ring cleavage of the $C_8H_8SiMe_3$ ligand has occurred; an *X*-ray investigation has therefore been carried out on $[Ru_2(C_8H_8SiMe_3)(SiMe_3)(CO)_4]$, reported herein, and has established the molecular structure as (7). A preliminary report of both structural studies has been given;[4] details of the synthetic studies are in refs. 3 and 5.



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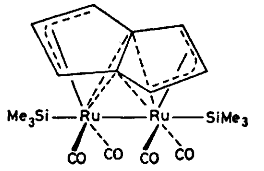

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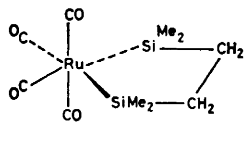

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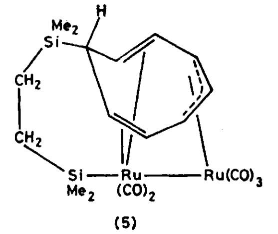

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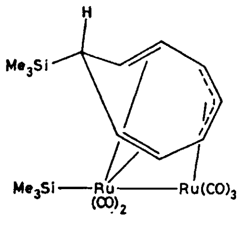

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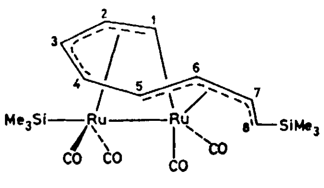

(7)

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† Pentacarbonyl-μ-{2′—3′-η,7′—8′-η: 4′—6′-η-[4-(cyclo-octa-2′,5′,7′-triene-1′,4′-diyl)-1,1,4,4-tetramethyl-1,4-disilapentyl]}-diruthenium (*Ru–Ru*) and tetracarbonyl(trimethylsilyl)-μ-[1—4-η:1-σ,5—8-η-(8-trimethylsilylocta-1,3,5,7-tetraenyl)]diruthenium (*Ru–Ru*).

EXPERIMENTAL

Compound (5).—Crystals of $[Ru_2(C_8H_8SiMe_2CH_2CH_2SiMe_2)(CO)_5]$ (5) grow as yellow prisms; the one chosen for data collection was of dimensions 0.17 × 0.30 × 0.32 mm and was sealed into a Lindemann capillary tube with epoxy resin. Intensities were collected to $2\theta = 55°$ according to methods described earlier,[6] with a variable scan rate dependent on a 2 s sampling of the peak intensity (c): scan rate = $0.0005c$ °s^{-1} for $110 \leqslant c \leqslant 1\,100$; 0.49° s^{-1} for $c > 1\,100$; or 0.03° s^{-1} for $c < 110$. Three check reflections, which were remeasured every 30 reflections, showed only random fluctuations during the 130 h of exposure of the crystal to X-rays. Of the total 4 557 independent measured intensities, 4 347 satisfied the criterion $I > 1.75\sigma(I)$, and only these were used in the solution and refinement of the structure. The intensities were corrected for Lorentz, polarisation, and X-ray absorption effects (with A^* ranging from 1.486 to 1.250).

TABLE 1

Atomic positional parameters for (5) (fractional co-ordinates) with estimated standard deviations in parentheses

Atom	x	y	z
Ru(1)	0.786 44(3)	0.902 77(4)	0.663 52(3)
Ru(2)	0.809 09(4)	0.669 09(5)	0.463 44(4)
Si(1)	0.641 0(1)	0.733 1(2)	0.914 5(1)
Si(2)	0.765 6(1)	1.105 0(2)	0.825 9(1)
C(1)	0.685 8(5)	0.690 5(6)	0.774 9(5)
C(2)	0.618 6(4)	0.777 8(6)	0.677 2(5)
C(3)	0.608 0(4)	0.736 2(6)	0.554 9(5)
C(4)	0.637 9(5)	0.593 0(6)	0.491 5(5)
C(5)	0.730 2(6)	0.499 9(6)	0.537 4(6)
C(6)	0.847 2(5)	0.557 5(6)	0.626 6(5)
C(7)	0.882 6(5)	0.688 3(6)	0.731 3(5)
C(8)	0.817 5(4)	0.744 6(6)	0.804 0(4)
C(9)	0.656 0(7)	0.949 9(8)	0.971 7(7)
C(10)	0.765 0(7)	1.054 4(8)	0.974 5(6)
C(11)	0.478 7(7)	0.656 5(11)	0.867 6(8)
C(12)	0.742 3(7)	0.636 3(9)	1.033 7(6)
C(13)	0.624 0(7)	1.205 0(9)	0.768 9(7)
C(14)	0.893 1(7)	1.273 5(9)	0.884 0(8)
C(01)	0.820 7(5)	0.502 5(7)	0.340 4(5)
O(01)	0.832 7(5)	0.405 7(7)	0.267 0(5)
C(02)	0.970 7(6)	0.763 0(7)	0.504 1(6)
O(02)	1.068 5(4)	0.812 8(7)	0.527 1(5)
C(03)	0.734 6(6)	0.800 4(8)	0.350 8(6)
O(03)	0.690 2(5)	0.875 8(7)	0.283 4(5)
C(04)	0.943 1(5)	1.004 3(7)	0.707 4(6)
O(04)	1.039 4(5)	1.066 2(7)	0.733 4(5)
C(05)	0.716 9(5)	1.037 6(6)	0.558 8(5)
O(05)	0.669 3(5)	1.117 5(6)	0.494 6(5)
H(1)	0.664(8)	0.621(10)	0.803(8)
H(2)	0.540(8)	0.843(11)	0.681(9)
H(3)	0.547(8)	0.775(11)	0.498(8)
H(4)	0.508(8)	0.553(11)	0.417(9)
H(5)	0.704(8)	0.392(11)	0.486(8)
H(6)	0.900(8)	0.502(11)	0.641(9)
H(7)	0.981(8)	0.707(11)	0.778(8)
H(8)	0.861(8)	0.782(11)	0.881(9)
H(91)	0.656(8)	0.967(11)	1.040(9)
H(92)	0.585(8)	1.000(11)	0.925(9)
H(101)	0.764(8)	1.181(11)	1.030(9)
H(102)	0.854(8)	1.014(11)	1.014(8)
H(111)	0.448(8)	0.707(11)	0.821(9)
H(112)	0.453(8)	0.687(11)	0.937(9)
H(113)	0.475(8)	0.570(11)	0.848(8)
H(121)	0.728(8)	0.650(11)	1.081(8)
H(122)	0.832(8)	0.669(11)	1.059(9)
H(123)	0.731(8)	0.533(11)	1.012(9)
H(131)	0.613(8)	1.279(11)	0.832(9)
H(132)	0.540(8)	1.125(11)	0.743(9)
H(133)	0.631(8)	1.238(11)	0.701(9)
H(141)	0.973(8)	1.202(11)	0.938(9)
H(142)	0.865(8)	1.359(11)	0.944(9)
H(143)	0.894(8)	1.308(11)	0.816(9)

Crystal Data.—$C_{19}H_{24}O_5Ru_2Si_2$, $M = 590.8$, Triclinic, $a = 11.851(2)$, $b = 8.761(2)$, $c = 11.864(2)$ Å, $\alpha = 100.54(2)$, $\beta = 110.37(1)$, $\gamma = 92.25(1)°$, $U = 1\,128.3(4)$ Å^3 at 298 K, $D_m = 1.74$ g cm^{-3}, $Z = 2$, $D_c = 1.74$ g cm^{-3}, $F(000) = 588$,

TABLE 2

Bond lengths (Å) and angles (°) for (5)

(*a*) Distances

Ru(1)–Ru(2)	2.9340(5)	Si(2)–C(1)	1.888(6)
Ru(1)–C(2)	2.302(6)	C(1)–C(2)	1.515(8)
Ru(1)–C(3)	2.331(5)	C(2)–C(3)	1.389(8)
Ru(1)–C(7)	2.357(5)	C(3)–C(4)	1.463(8)
Ru(1)–C(8)	2.301(6)	C(4)–C(5)	1.406(8)
Ru(2)–C(4)	2.263(6)	C(5)–C(6)	1.423(8)
Ru(2)–C(5)	2.187(7)	C(6)–C(7)	1.453(7)
Ru(2)–C(6)	2.242(6)	C(7)–C(8)	1.386(8)
Ru(1)–Si(1)	2.461(2)	C(8)–C(1)	1.512(7)
Si(1)–C(13)	1.883(8)	Si(2)–C(11)	1.865(8)
Si(1)–C(14)	1.924(8)	Si(2)–C(12)	1.870(8)
Si(1)–C(10)	1.893(8)	Si(2)–C(9)	1.876(7)
Ru(2)–C(01)	1.912(6)	C(9)–C(10)	1.541(12)
Ru(2)–C(02)	1.915(7)	C(01)–O(01)	1.150(9)
Ru(2)–C(03)	1.927(7)	C(02)–O(02)	1.142(8)
Ru(1)–C(04)	1.881(6)	C(03)–O(03)	1.131(9)
Ru(1)–C(05)	1.876(6)	C(04)–O(04)	1.156(8)
		C(05)–O(05)	1.147(8)

(*b*) Angles

(*i*) The co-ordination around Ru(1)

Ru(2)–Ru(1)–Si(1)	177.90(4)
Ru(2)–Ru(1)–C(2,3) *	82.7(1)
Ru(2)–Ru(1)–C(7,8) *	81.9(1)
Ru(2)–Ru(1)–C(04)	93.7(2)
Ru(2)–Ru(1)–C(05)	93.0(2)
C(2,3) *–Ru(1)–C(04)	161.2(2)
C(2,3) *–Ru(1)–C(05)	93.8(2)
Si(1)–Ru(1)–C(2,3) *	97.5(1)
Si(1)–Ru(1)–C(7,8) *	100.2(1)
Si(1)–Ru(1)–C(04)	86.4(2)
Si(1)–Ru(1)–C(05)	84.9(2)
C(04)–Ru(1)–C(05)	92.3(3)
C(7,8) *–Ru(1)–C(04)	94.0(2)
C(7,8) *–Ru(1)–C(05)	161.0(3)
C(7,8) *–Ru(1)–C(2,3) *	80.1(2)

(*ii*) The co-ordination around Ru(2)

Ru(1)–Ru(2)–C(01)	174.8(2)	Ru(1)–Ru(2)–C(4)	72.5(1)
Ru(1)–Ru(2)–C(02)	89.0(2)	Ru(1)–Ru(2)–C(5)	85.3(2)
Ru(1)–Ru(2)–C(03)	88.9(2)	Ru(1)–Ru(2)–C(6)	72.9(1)
C(01)–Ru(2)–C(02)	93.7(3)	C(01)–Ru(2)–C(4)	103.9(2)
C(01)–Ru(2)–C(03)	95.3(3)	C(01)–Ru(2)–C(5)	89.6(3)
C(02)–Ru(2)–C(03)	94.8(3)	C(01)–Ru(2)–C(6)	102.3(2)
C(02)–Ru(2)–C(4)	158.5(2)	C(03)–Ru(2)–C(4)	95.6(3)
C(02)–Ru(2)–C(5)	133.4(3)	C(03)–Ru(2)–C(5)	131.2(3)
C(02)–Ru(2)–C(6)	96.9(3)	C(03)–Ru(2)–C(6)	158.1(3)

(*iii*) The $C_8H_8SiMe_2CH_2CH_2SiMe_2$ moiety

C(1)–C(2)–C(3)	123.8(5)	C(1)–Si(2)–C(9)	109.4(3)
C(2)–C(3)–C(4)	128.5(5)	C(1)–Si(2)–C(11)	108.4(3)
C(3)–C(4)–C(5)	129.1(4)	C(1)–Si(2)–C(12)	107.8(3)
C(4)–C(5)–C(6)	125.0(5)	C(9)–Si(2)–C(11)	108.0(4)
C(5)–C(6)–C(7)	129.4(6)	C(9)–Si(2)–C(12)	111.4(3)
C(6)–C(7)–C(8)	128.6(5)	C(11)–Si(2)–C(12)	111.8(4)
C(7)–C(8)–C(1)	123.9(4)	Ru(1)–Si(1)–C(10)	120.3(2)
C(8)–C(1)–C(2)	103.5(5)	Ru(1)–Si(1)–C(13)	112.5(2)
C(8)–C(1)–Si(2)	112.5(3)	Ru(1)–Si(1)–C(11)	111.7(3)
C(2)–C(1)–Si(2)	112.4(4)	C(10)–Si(1)–C(13)	105.2(4)
Si(2)–C(9)–C(10)	120.3(6)	C(10)–Si(1)–C(14)	102.1(4)
C(9)–C(10)–Si(1)	118.7(4)	C(13)–Si(1)–C(14)	103.4(3)

(*iv*) The carbonyl groups

Ru(2)–C(01)–O(01)	176.9(6)	Ru(1)–C(04)–O(04)	179.4(6)
Ru(2)–C(02)–O(02)	177.1(6)	Ru(1)–C(05)–O(05)	176.9(6)
Ru(2)–C(03)–O(03)	179.1(5)		

* C(x,y) is the midpoint between C(x) and C(y).

space group $P\bar{1}$, Mo-K_α X-radiation, $\lambda = 0.710\,69$ Å, μ(Mo-K_α) = 14.4 cm^{-1}.

Structure Solution and Refinement.—The two ruthenium atoms were located from a Patterson synthesis assuming space group $P\bar{1}$, and from the positions so derived all other non-hydrogen atoms were located by successive electron-density (e.d.) difference syntheses. The structure was refined (excluding H atoms) by full-matrix least squares with anisotropic thermal parameters for all atoms, to R 0.105 (R' 0.095). Hydrogen atoms were then incorporated from e.d. difference maps and the structure refined by blocked-matrix least squares, allowing positional and isotropic thermal parameters to refine for the hydrogen atoms. A weighting scheme of the form $w^{-1} = a + b|F_o| + c|F_o|^2$, with $a = 1.31$, $b = -0.043\,5$, and $c = 0.001\,44$ gave a satisfactory weight analysis. Refinement converged at R 0.046 (R' 0.062), and in the final cycle the mean shift-to-error ratio was 0.003 : 1. The final e.d. difference synthesis showed no peaks >0.7 e Å^{-3} and the highest peaks were in the neighbourhood of the Ru atoms. Atomic scattering factors were from ref. 7 for all non-hydrogen atoms; those for Ru and Si were corrected for the effects of anomalous dispersion [8] (Ru: $\Delta f'$ −1.2, $\Delta f''$ 6.6; Si: $\Delta f'$ 0.1, $\Delta f''$ 0.1). Scattering factors for hydrogen were from ref. 9. Positional parameters are in Table 1, interatomic distances and bond angles in Table 2, and relevant least-squares planes in Table 3. All thermal parameters, and the list of observed and calculated structure factors for

TABLE 3

Equations of some least-squares planes for (5) and distances (Å) of relevant atoms from planes in square brackets

Plane (1): C(1), C(2), C(3), C(4)
$10.2338x + 3.8875y - 2.9325z = 3.7767$
[C(1) −0.019, C(2) 0.043, C(3) −0.045, C(4) 0.020]

Plane (2): C(1), C(8), C(7), C(6)
$1.5355x - 7.0138y + 7.7519z = 0.0417$
[C(1) 0.015, C(8) −0.034, C(7) 0.036, C(6) −0.016]

Plane (3): C(3), C(4), C(5), C(6), C(7)
$-7.1394x - 4.8878y + 9.7857z = 0.2986$
[C(3) −0.031, C(4) 0.102, C(5) −0.142, C(6) 0.102, C(7) −0.031]

Angles (°) between least-squares planes:

(1)–(2)	80.0	(2)–(3)	44.9
(1)–(3)	44.7		

TABLE 4

Atomic positional parameters for (7) (fractional co-ordinates) with estimated standard deviations in parentheses

Atom	x	y	z
Ru(1)	0.413 80(11)	1.045 66(10)	0.322 30(3)
Ru(2)	0.531 26(12)	0.957 54(11)	0.214 03(3)
Si(1)	0.361 7(5)	1.178 0(5)	0.410 5(1)
C(11)	0.236 0(24)	0.984 0(25)	0.460 7(6)
C(12)	0.168 1(21)	1.289 5(21)	0.404 1(7)
C(13)	0.622 7(22)	1.367 8(21)	0.442 2(5)
C(1)	0.725 7(15)	1.137 5(15)	0.278 0(5)
C(2)	0.726 7(17)	1.308 5(16)	0.303 5(5)
C(3)	0.547 6(19)	1.355 7(14)	0.297 4(6)
C(4)	0.372 0(18)	1.254 2(16)	0.259 7(4)
C(5)	0.373 8(18)	1.157 4(16)	0.208 2(5)
C(6)	0.564 2(20)	1.223 5(17)	0.176 4(5)
C(7)	0.578 9(20)	1.097 6(18)	0.137 2(5)
C(8)	0.403 0(21)	0.905 4(17)	0.128 2(5)
Si(2)	0.412 5(8)	0.717 2(6)	0.077 2(2)
C(21)	0.256 9(43)	0.471 5(27)	0.104 3(9)
C(22)	0.280 0(33)	0.726 9(25)	0.012 7(8)
C(23)	0.701 2(40)	0.770 6(41)	0.063 1(8)
C(01)	0.484 3(19)	0.878 5(17)	0.362 9(5)
O(01)	0.529 2(19)	0.780 7(17)	0.388 3(5)
C(02)	0.117 5(17)	0.892 8(16)	0.330 8(5)
O(02)	−0.064 8(12)	0.795 7(13)	0.335 9(4)
C(03)	0.721 6(17)	0.842 0(16)	0.210 7(6)
O(03)	0.837 7(16)	0.772 2(16)	0.208 5(5)
C(04)	0.296 4(18)	0.721 3(15)	0.234 8(5)
O(04)	0.153 2(15)	0.574 4(12)	0.242 8(4)

TABLE 5

Bond lengths (Å) and angles (°) for (7)

(*a*) Distances

Ru(1)–Ru(2)	2.908(1)	Si(1)–C(11)	1.86(2)
Ru(1)–Si(1)	2.439(4)	Si(1)–C(12)	1.89(2)
Ru(1)–C(01)	1.88(1)	Si(1)–C(13)	1.88(1)
Ru(1)–C(02)	1.87(1)	C(01)–O(01)	1.14(2)
Ru(2)–C(03)	1.88(1)	C(02)–O(02)	1.15(1)
Ru(2)–C(04)	1.91(1)	C(03)–O(03)	1.15(2)
Ru(1)–C(1)	2.24(1)	C(04)–O(04)	1.14(1)
Ru(1)–C(2)	2.27(1)	Ru(2)–C(1)	2.08(1)
Ru(1)–C(3)	2.24(1)	Ru(2)–C(2)	3.18(1)
Ru(1)–C(4)	2.37(1)	Ru(2)–C(5)	2.25(1)
C(1)–C(2)	1.42(2)	Ru(2)–C(6)	2.19(1)
C(2)–C(3)	1.44(2)	Ru(2)–C(7)	2.16(1)
C(3)–C(4)	1.42(2)	Ru(2)–C(8)	2.23(1)
C(4)–C(5)	1.44(2)	C(8)–Si(2)	1.89(1)
C(5)–C(6)	1.42(2)	Si(2)–C(21)	1.86(2)
C(6)–C(7)	1.37(2)	Si(2)–C(22)	1.84(2)
C(7)–C(8)	1.44(1)	Si(2)–C(23)	1.88(3)

(*b*) Angles

(*i*) The co-ordination around Ru(1)

C(01)–Ru(1)–C(02)	92.3(5)	C(1)–Ru(1)–Si(1)	126.7(3)
Ru(2)–Ru(1)–C(01)	99.2(4)	C(1)–Ru(1)–C(01)	89.1(5)
Ru(2)–Ru(1)–C(02)	108.5(4)	C(1)–Ru(1)–C(02)	153.7(4)
Si(1)–Ru(1)–C(01)	86.1(4)	C(3,4) *–Ru(1)–Ru(2)	78.3(3)
Si(1)–Ru(1)–C(02)	79.6(4)	C(3,4) *–Ru(1)–Si(1)	93.5(3)
Si(1)–Ru(1)–Ru(2)	170.0(1)	C(3,4) *–Ru(1)–C(01)	155.7(5)
C(1)–Ru(1)–C(3,4) *	74.5(4)	C(3,4) *–Ru(1)–C(02)	108.3(5)
C(1)–Ru(1)–Ru(2)	45.4(3)		

(*ii*) The co-ordination around Ru(2)

C(03)–Ru(2)–C(04)	92.1(5)
Ru(1)–Ru(2)–C(03)	117.1(4)
Ru(1)–Ru(2)–C(04)	74.8(4)
Ru(1)–Ru(2)–C(1)	50.0(3)
Ru(1)–Ru(2)–C(5,6) *	83.4(3)
Ru(1)–Ru(2)–C(7,8) *	135.9(4)
C(7,8) *–Ru(2)–C(03)	102.5(6)
C(7,8)–Ru(2)–C(04)	109.5(4)
C(1)–Ru(2)–C(03)	87.1(5)
C(1)–Ru(2)–C(04)	115.7(4)
C(1)–Ru(2)–C(5,6) *	88.0(4)
C(1)–Ru(2)–C(7,8) *	133.1(4)
C(5,6) *–Ru(2)–C(03)	147.1(5)
C(5,6) *–Ru(2)–C(04)	118.8(5)
C(5,6) *–Ru(2)–C(7,8) *	61.3(5)

(*iii*) The SiMe$_3$ ligand

Ru(1)–Si(1)–C(11)	111.7(6)	C(11)–Si(1)–C(12)	105.1(8)
Ru(1)–Si(1)–C(12)	111.3(5)	C(11)–Si(1)–C(13)	107.4(6)
Ru(1)–Si(1)–C(13)	112.5(5)	C(12)–Si(1)–C(13)	108.5(7)

(*iv*) The C$_8$–SiMe$_3$ moiety

Ru(1)–C(1)–Ru(2)	84.6(3)	Ru(2)–C(1)–C(2)	129.5(9)
Ru(1)–C(1)–C(2)	72.6(6)	C(7)–C(8)–Si(2)	123.3(10)
C(1)–C(2)–C(3)	122.1(9)	C(8)–Si(2)–C(21)	108.8(9)
C(2)–C(3)–C(4)	123.4(12)	C(8)–Si(2)–C(22)	108.7(9)
C(3)–C(4)–C(5)	128.0(12)	C(8)–Si(2)–C(23)	110.3(9)
C(4)–C(5)–C(6)	120.9(9)	C(21)–Si(2)–C(22)	108.0(9)
C(5)–C(6)–C(7)	118.1(9)	C(21)–Si(2)–C(23)	112.0(14)
C(6)–C(7)–C(8)	120.1(11)	C(22)–Si(2)–C(23)	109.0(9)

(*v*) The carbonyl groups

Ru(1)–C(01)–O(01)	178.5(10)	Ru(2)–C(05)–O(03)	179.8(10)
Ru(1)–C(02)–O(02)	178.8(12)	Ru(2)–C(04)–O(04)	174.3(10)

* C(x,y) is the midpoint between C(x) and C(y).

this compound and (7), are in Supplementary Publication No. SUP 22683 (35 pp.).*

Compound (7).—Crystals of $[Ru_2(C_8H_8SiMe_3)(SiMe_3)(CO)_4]$ (7) grow as yellow rhomboids with well developed (001) faces. Intensities were collected from a crystal 0.40 × 0.38 × 0.09 mm, these dimensions being along the [210], [010], and [001] directions. Intensities were collected to $2\theta = 53°$ with a variable scan rate (see above) $= 0.000\ 14c°\ s^{-1}$ for $250 \leqslant c \leqslant 750$; $1.0°\ s^{-1}$ for $c > 750$; or $0.03°\ s^{-1}$ for $c < 250$. There was no deterioration of the crystal over 120 h exposure to *X*-rays. Of the total 4 268 reflections, 3 485 satisfied the criterion $I > 1.75\sigma(I)$ and only these were used.

TABLE 6

Equations of some least-squares planes for (7) and distances (Å) of the relevant atoms from planes in square brackets

Plane (1): C(1), C(2), C(3), C(4)
$-1.9197x - 3.1585y + 19.0081z = 0.2798$
[C(1) 0.019, C(2) −0.039, C(3) 0.039, C(4) −0.019]

Plane (2): C(3), C(4), C(5), C(6)
$3.1789x - 7.2107y + 9.1844z = -5.3584$
[C(3) 0.055, C(4) −0.118, C(5) 0.113, C(6) −0.050]

Plane (3): C(5), C(6), C(7), C(8)
$4.4202x - 4.7905y + 16.7761z = -0.4029$
[C(5) 0.003, C(6) −0.005, C(7) 0.005, C(8) −0.003]

Angles (°) between least-squares planes

(1)–(2)	51.9	(2)–(3)	33.7
(1)–(3)	56.6		

Some torsion angles (°) in the C_8 chain

Ru(2)–C(1)–C(2)–C(3)	−17.0	C(4)–C(5)–C(6)–C(7)	161.0
C(1)–C(2)–C(3)–C(4)	−9.6	C(5)–C(6)–C(7)–C(8)	−1.2
C(2)–C(3)–C(4)–C(5)	−150.9	C(6)–C(7)–C(8)–Si(2)	−177.3
C(3)–C(4)–C(5)–C(6)	−29.9		

Crystal Data.—$C_{18}H_{26}O_4Ru_2Si_2$, $M = 564.8$, Triclinic, $a = 6.903(3)$, $b = 7.669(3)$, $c = 24.454(10)$ Å, $\alpha = 92.41(3)$, $\beta = 89.87(3)$, $\gamma = 116.45(3)°$, $U = 1\ 157.8(8)$ Å^3 at 293 K, $D_m = 1.615$ g cm^{-3}, $Z = 2$, $D_c = 1.620$ g cm^{-3}, $F(000) = 564$, space group $P\bar{1}$, Mo-K_α *X*-radiation, $\bar{\lambda} = 0.710\ 69$ Å, μ(Mo-K_α) = 13.9 cm^{-1}.

TABLE 7

Selected intermolecular contact distances for (7)

Atom i	Atom j	Vector from molecule containing i to molecule containing j	Contacts (Å)
C(1)	O(04)	$1 + x, 1 + y, z$	3.48(1)
C(2)	O(02)	$1 + x, 1 + y, z$	3.41(1)
O(03)	C(04)	$1 + x, y, z$	3.42(2)
O(03)	O(04)	$1 + x, y, z$	3.29(2)
C(4)	O(04)	$x, 1 + y, z$	3.45(2)
O(02)	C(01)	$x - 1, y, z$	3.50(2)
O(02)	O(01)	$x - 1, y, z$	3.04(2)
O(02)	C(3)	$x - 1, y - 1, z$	3.34(1)

Structure Solution and Refinement.—The structure was solved by heavy-atom methods and electron-density difference syntheses. It was not possible, however, to locate the hydrogen atoms directly, so these were incorporated at calculated positions (C–H 0.95 Å).† The structure was refined by blocked-matrix least squares, with anisotropic thermal parameters for all non-hydrogen atoms and with fixed parameters ($U_H = 1.10\ U_c$) for the H atoms.

A weighting scheme (as above) with $a = 2.50$, $b = -0.136$, and $c = 0.003\ 19$ gave a satisfactory weight analysis. Refinement converged at R 0.055 (R' 0.069), with all other details as for (5). Positional parameters are in Table 4, interatomic distances and bond angles in Table 5, relevant least-squares planes, interplanar angles, and torsion angles in Table 6, and selected intermolecular contacts in Table 7.

DISCUSSION

$[Ru_2(C_8H_8SiMe_2CH_2CH_2SiMe_2)(CO)_5]$.—The molecular configuration of (5) is illustrated in Figure 1 which also shows the crystallographic numbering sequence. Like many other diruthenium carbonyl derivatives, it contains an almost linear spine with the 'saw-horse' configuration of eclipsed orthogonal carbonyl groups. The two ruthenium atoms are bridged symmetrically by the C_8 ring, in that the plane through the spine which bisects the equatorial carbonyl directions is also a mirror plane for the C_8 ring [atoms C(1) and C(5) lie in the mirror plane]. Three of the eight ring atoms [C(4)—C(6)] are η^3-bonded to Ru(2), while C(2), C(3) and C(7), C(8) form a diene η^4 attachment, again symmetrically related to the mirror plane. This symmetrical mode of attachment of a C_8 ring to a dimetal nucleus has not been observed before,‡ but is believed also to occur in the complex $[Ru_2(C_8H_8SiMe_3)(SiMe_3)(CO)_5]$ (6) by inference from the strikingly similar spectroscopic properties of (6) and (5). Returning to (5), atom C(1) is linked *via* a further ring to Si(1), the chain comprising Si(2), C(9), and C(10). The tetrahedral valence angles around C(1) naturally require Si(2) to lie in the mirror plane of the C_8 ring, but C(9) and C(10) both lie to the same side of this plane and hence destroy any mirror symmetry for the molecule as a whole [as also do the attendant methyl groups on Si(1) and Si(2)].

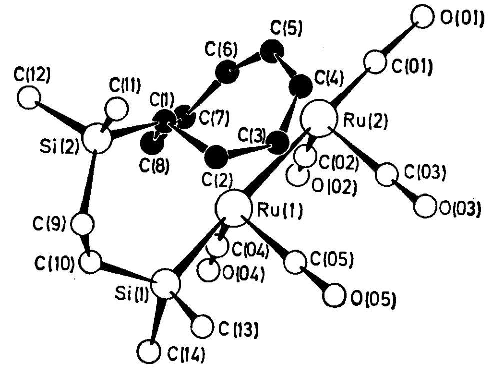

FIGURE 1 Molecular structure of $[Ru_2(C_8H_8SiMe_2CH_2CH_2SiMe_2)(CO)_5]$, (5), showing the crystallographic numbering sequence

The Ru–Ru distance (2.934 Å) is rather long for a single bond, but is similar to that found in $[Ru_2(C_7H_6SiMe_3)(SiMe_3)(CO)_5]$ [11] (2.937 Å) and in $[Ru_2(SnMe_3)_2(CO)_8]$ [12] (2.943 Å). In contrast, the Ru–Si bond

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* For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1979, Index issue.

† These positions have not been tabulated.

‡ Since our first paper on this work was published,[4] a similar mode of bonding between a C_8 ring and another dimetal species has been established, *viz.* for $[Rh_2(C_8H_9)_2(C_8H_{12})]$,[10] cycloocta-1,5-diene-μ-(3—5-η : 1—2,6—7-η-cyclo-octatrienyl)-(3—5-η-cyclo-octatrienyl)dirhodium.

(2.461 Å) is rather short if the radius of Si (sp^3) is taken as 1.17 Å and that of Ru {from $[Ru_3(CO)_{12}]$} as 1.42 Å. The Ru–Si–C angles are also all larger than the ideal tetrahedral angle, suggesting some enhancement of the Ru–Si bond order. The carbon chain between Si(1) and Si(2) shows bond angles at the two C atoms of *ca.* 120°, probably imposed by the stereochemical relationships within the molecule, but the mean Si–C distance [1.886(7) Å] is not significantly different from the sum of the covalent radii for sp^3 C and Si. Within the C_8 ring the bond lengths are determined sufficiently accurately to show that the formal bonding description given above is substantially correct.

The Ru–C(carbonyl) bond distances are not equal, those *trans* to the C=C double bonds in the C_8 ring, attached to Ru(1), being significantly shorter than those attached to Ru(2). The fact that the C–O distances do not seem to follow an inverse pattern is merely due to the insensitivity of bond lengths as a measure of bond order for bonds of order 2—3. The packing of the molecules in the unit cell is shown in Figure 2; the packing is such as to make all the carbonyl groups mutually parallel or orthogonal. There are no significantly short intermolecular contacts.

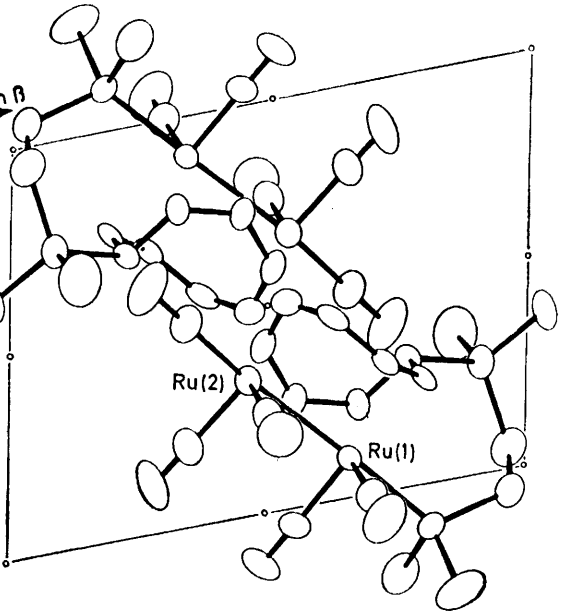

FIGURE 2 Contents of the triclinic unit cell of (5), viewed in projection down *a*

$[Ru_2(C_8H_8SiMe_3)(SiMe_3)(CO)_4]$.—The molecular configuration of (7) is illustrated in Figure 3 which also shows the crystallographic numbering sequence. The structure is highly unusual. Although the spinal sequence $Me_3SiRu(CO)_2Ru(CO)_2$ of structure (5) is retained, the carbonyl groups are no longer in an eclipsed configuration; one $Ru(CO)_2$ unit is twisted relative to the other so that neither the planes of these units, nor the individual Ru–C–O directions, are parallel. The CO ligands on any one Ru atom do, however, remain orthogonal to each other. The C_8 ring has opened to form a contorted chain C(1)—C(8) carrying a terminal $SiMe_3$ group on C(8) but with C(1) directly σ-bonded to Ru(2). Within this chain, atoms C(1)—C(4) are coplanar (Table 6) and form a diene-type unit η^4-bonded to Ru(1), while atoms C(5)—C(8) are similarly coplanar and are bonded to Ru(2). The bond lengths within the C_8 chain are all close to the mean value of 1.42 Å, suggesting extensive delocalisation of the π interactions, but the atom sequence C(3)—C(6), although itself coplanar, shows considerable twist relative to the other diene units (Table 6). Torsion angles within the chain are also included in Table 6.

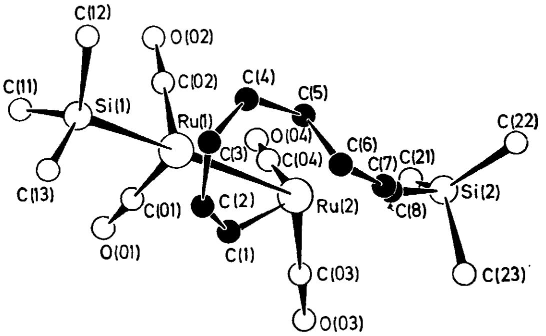

FIGURE 3 Molecular structure of $[Ru_2(C_8H_8SiMe_3)(SiMe_3)(CO)_4]$, (7), showing the crystallographic numbering sequence

Both ruthenium atoms show distorted octahedral coordination, but that of Ru(2) is particularly strained by the acuteness of the angle between Ru(2)–Ru(1) and Ru(2)–C(1) (*ca.* 50°). The distortion also shows particularly in the bonding of the carbonyl C(04)–O(04), where the angle Ru(1)–Ru(2)–C(04) is *ca.* 75°. The acuteness of this angle seems unlikely to be caused by intermolecular forces, as contacts involving C(04) and O(04) (Table 7) are not among the closest. Significantly, the Ru(1)–Ru(2) distance of 2.908 Å is shorter than that found in (5) (2.934 Å). The Ru–Ru–Si sequence is significantly non-linear (170.0°) with the $SiMe_3$ group bending towards the diene. This contrasts with $[Ru_2(SiMe_3)(CO)_5(C_7H_7SiMe_3)]$ [11] for which the deviation is away from the C_7 ring (173°). The Ru(1)–Si(1) bond length (2.439 Å) is rather short for a single bond (see above) and the Ru–Si–C angles are all greater than the ideal tetrahedral value.

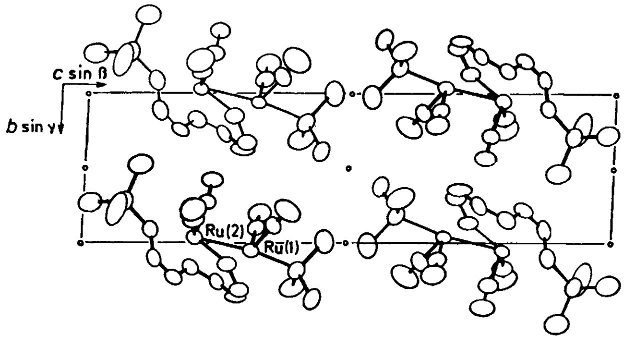

FIGURE 4 Contents of the triclinic unit cell of (7) viewed in projection down *a*

In contrast, the $SiMe_3$ group attached to C(8) has angles which are all regular; this is commonly found. The mean Ru–C and C–O distances for the carbonyl ligands are 1.89 and 1.15 Å, both of which are within ranges commonly observed. The contents of the triclinic unit cell are shown in Figure 4.

The novel opening of the C_8 ring which occurs on thermolysis of (6) is not parallelled in (5) where the Si atoms are bonded to one another *via* a carbon chain. Our structural study shows that ring opening results in considerable spatial separation of the trimethylsilyl groups, a separation which would be impossible for (5).

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