The Opening of a C_8 Ring in a Di-ruthenium Complex; Crystal and Molecular Structures of $[Ru_2(CO)_5\{Me_2SiCH_2CH_2Si(Me_2)C_8H_8\}]$ and $[Ru_2(SiMe_3)(CO)_4(C_8H_8SiMe_3)]$

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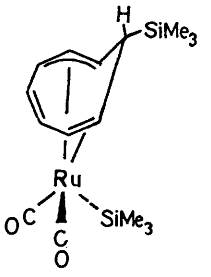
Summary The binuclear ruthenium complexes $[Ru_2(SiMe_3)(CO)_5(C_8H_8SiMe_3)]$ and $[Ru_2(CO)_5\{Me_2SiCH_2CH_2Si(Me_2)C_8H_8\}]$ contain cyclic η^7-C_8 ligands; the former on thermolysis affords $[Ru_2(SiMe_3)(CO)_4(C_8H_8SiMe_3)]$, shown by *X*-ray diffraction to contain a ring-opened η^8-C_8 ligand.

TREATMENT of $[Ru(SiMe_3)_2(CO)_4]$ with cyclo-octatetraene is known[1] to yield initially the migration product (**1**), which subsequently decomposes to give the pentalene complex $[Ru_2(SiMe_3)_2(CO)_4(C_8H_6)]$.[2] In an extension of studies on the migration of trimethylsilyl groups from ruthenium to co-ordinated hydrocarbons, the complex (**2**)[3] was treated with cyclo-octatetraene. Among the products was yellow crystalline $[Ru_2(CO)_5\{Me_2SiCH_2CH_2Si(Me_2)C_8H_8\}]$ [**3**; m.p. 175 °C decomp.; ν_{CO} 2056s, 2002s, 2000sh, 1976w, 1955w cm^{-1}]. The ^1H n.m.r. spectrum [τ 5·46 (1H, t), 6·06 (2H, dd), 7·13 (2H, dd), 7·82 (2H, dd), 8·50—9·30 (5H, m), 9·56 (6H, s), 10·00 (6H, s)], in contrast to that of (**1**), was unchanged at −60 °C, and indicated that one (τ 10·00) of the $SiMe_2$ groups had migrated to carbon while the other (τ 9·56) had remained bonded to ruthenium. That the ring-to-metal bonding was of a new type was unequivocally established by a single crystal *X*-ray diffraction study.



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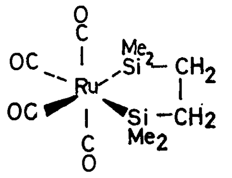

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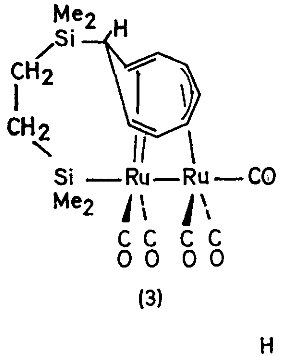

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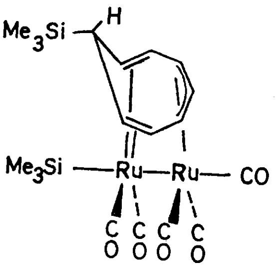

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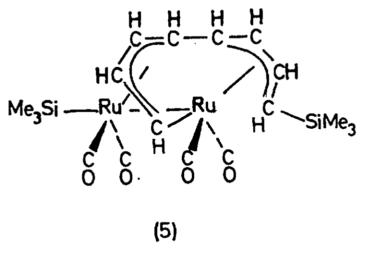

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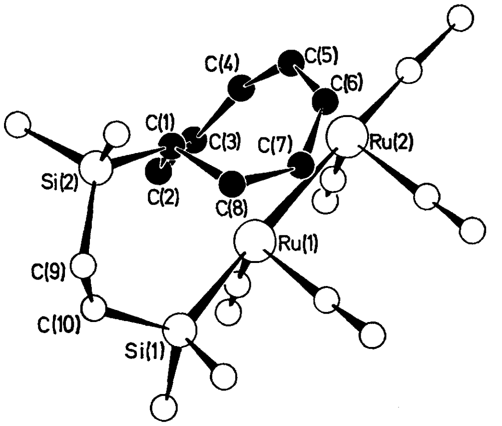

FIGURE 1. Molecular structure of $[Ru_2(CO)_5\{Me_2SiCH_2CH_2Si(Me_2)C_8H_8\}]$. Ru(1)–Ru(2) = 2·935(2), Ru(1)–Si(1) = 2·458(4), Ru(2)–C(4—6) (mean) = 2·24(2), Ru(1)–C(7,8,2,3) (mean) = 2·34(2), C(1)–Si(2) = 1·90(1), Si–C_{Me} (mean) = 1·90(2), Ru–C(carbonyl) (mean) = 1·90(1), C–O (mean) = 1·15(2) Å.

Crystal data: $C_{19}H_{24}O_5Si_2Ru_2$, $M = 590\cdot75$, triclinic, space group $P\bar{1}$, $a = 11\cdot851(2)$, $b = 8\cdot761(2)$, $c = 11\cdot864(2)$ Å, $\alpha = 100\cdot54(2)$, $\beta = 110\cdot37(1)$, $\gamma = 92\cdot25(1)°$, $Z = 2$, $D_c = 1\cdot68\ g\ cm^{-3}$; Mo-$K_\alpha$ *X*-radiation ($\bar{\lambda} = 0\cdot71069$ Å), $\mu = 14\cdot3\ cm^{-1}$. Data were collected on a Syntex $P2_1$ four-circle diffractometer (to $2\theta = 55°$); the structure was solved by conventional heavy atom methods and refined with anisotropic thermal parameters for all non-hydrogen atoms. For 3658 independent reflections, $R = 0\cdot066$. The molecular structure of (**3**) (Figure 1) consists of a linear O–C–Ru–Ru–Si spine with two carbonyl groups attached orthogonally to each ruthenium atom in an eclipsed configuration. The two Ru atoms are bridged symmetrically (relative to the plane through the spine bisecting the axial carbonyl direction) by the C_8 ring; three of the eight ring atoms {C(4)–C(6)} are η^3 bonded to Ru(2) so that C(5) lies in the 'mirror' plane, while C(2), C(3) and C(7), C(8) form a diene-type η^4 attachment to Ru(1), again symmetrically related to the 'mirror' which contains C(1). A further ring joins C(1) to Si(1) *via* Si(2), C(9) and C(10). The valence angles naturally require Si(2) to lie in the 'mirror', but C(9) and C(10) both lie to the same side of the plane and destroy the mirror symmetry for the molecule as a whole [as also, consequently, do the two attendant methyl groups on Si(1) and on Si(2)].

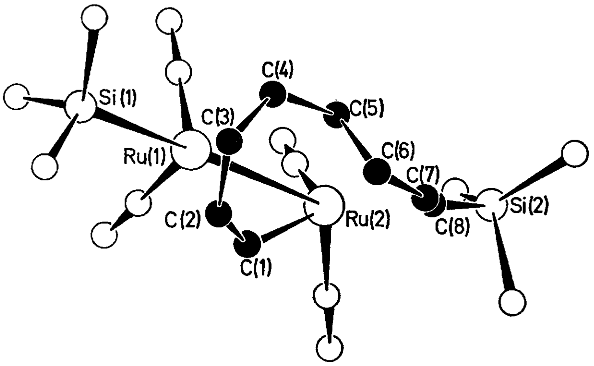

FIGURE 2. Molecular structure of [$Ru_2(SiMe_3)(CO)_4(C_8H_8SiMe_3)$]. Ru(1)–Ru(2) = 2·909(2), Ru(1)–Si(1) = 2·437(5), Ru(2)–C(1) = 2·10(1), Ru(1)–C(1—4) (mean) = 2·29(2), Ru(2)–C(5—8) (mean) = 2·22(2), C(8)–Si(2) = 1·921(2), Ru–C(carbonyl) (mean) = 1·89(1), C–O (mean) = 1·14(2) Å.

Establishment of the molecular structure of (**3**) provides insight into a minor product in the formation of (**1**), a yellow crystalline complex [$Ru_2(SiMe_3)(CO)_5(C_8H_8SiMe_3)$] [(**4**); m.p. 140 °C decomp.; ν_{CO} 2056s, 2003s, 1996s, 1940m cm^{-1}; τ 5·42 (1H, t), 6·04 (2H, dd), 6·23 (2H, t), 7·69 (2H, dd), 9·18 (1H, t), 9·76 (9H, s), 9·99 (9H, s)] which is obtained in good yield by heating (**1**) with [$Ru(SiMe_3)_2(CO)_4$], the latter acting as a tricarbonylruthenium source. The spectroscopic properties of (**4**) are almost identical with those of (**3**), strongly indicating the structure proposed.

Heating (**4**) in octane releases a molecule of CO with near quantitative formation of yellow crystalline [$Ru_2(SiMe_3)(CO)_4(C_8H_8SiMe_3)$] [(**5**); m.p. 120 °C; ν_{CO} 2033s, 1995m, 1976s, 1957m cm^{-1}]. The ^{13}C n.m.r. spectrum, with eight signals for the hydrocarbon {at 38·28, 42·59, 73·41, 79·72, 96·41, 99·86, 115·40, and 148·40 p.p.m. (downfield of Me_4Si)}, suggested that ring cleavage of the $C_8H_8SiMe_3$ ligand had occurred; an *X*-ray diffraction study was therefore undertaken.

Crystal data: $C_{18}H_{26}O_4Si_2Ru_2$, $M = 564·76$, triclinic, space group $P\bar{1}$, $a = 6·903(3)$, $b = 7·669(3)$, $c = 24·45(1)$ Å, $\alpha = 92·41(3)$, $\beta = 89·87(3)$, $\gamma = 116·45(3)°$, $Z = 2$ $D_c = 1·70$ g cm^{-3}; Mo-K_α *X*-radiation, ($\bar{\lambda} = 0·71069$ Å), $\mu = 14·0$ cm^{-1}. Data were collected (to $2\theta = 53°$) and refined as for (**2**). For 3600 independent reflections, $R = 0·070$.

The crystallographic investigation reveals a highly unusual structure (Figure 2). The spinal grouping $Me_3Si–Ru(CO)_2–Ru(CO)_2$ is retained but 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 C_8 ring has opened to form a chain C(1)–C(8) carrying an $SiMe_3$ group on C(8), but with C(1) directly σ-bonded to Ru(2). Atoms C(1)—C(4) are coplanar and form a diene-type unit η^4-bonded to Ru(1), while C(5)—C(8) are similarly related to Ru(2). The two diene groups are, however, independent of one another as judged by the length of the linking bond C(4)–C(5), 1·47 Å. The octahedral co-ordination of Ru(2) is particularly strained because of the acuteness of the angle between Ru(2)–Ru(1) and Ru(2)–C(1).

This novel opening of the C_8 ring in (**4**) is not parallelled by (**3**), which is stable in octane at reflux. This is readily attributable to the linking of the silicon atoms, since it can be seen that the ring-opening of (**4**) results in a considerable separation of the trimethylsilyl groups, a separation which would be impossible for (**3**).

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