Hydrocarbon Complexes of Iron, Ruthenium, and Osmium. Part 11.[1] Diruthenium Complexes of Pentalene derived from Cyclo-octatetraene: Crystal and Molecular Structure of the Fluxional Molecule Dicarbonyl-(trimethylsilyl)(1—3:6—7-η-8-*endo*-trimethylsilylcyclo-octatrienyl)-ruthenium, a Pentalene Precursor

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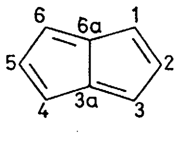
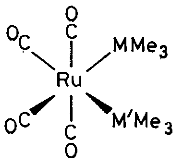
Cyclo-octatetraenes C_8H_7R (R = H, Me, Ph, or $SiMe_3$) react with $[Ru(SiMe_3)_2(CO)_4]$ in hexane at reflux to give trimethylsilyl migration products $[Ru(SiMe_3)(CO)_2\{C_8H_7R(SiMe_3)\}]$ and ring-closed tetrahydropentalenyl complexes $[Ru(SiMe_3)(CO)_2(C_8H_8R)]$. The molecular structure of complexes of the former type has been established by a single-crystal *X*-ray diffraction study of $[Ru(SiMe_3)(CO)_2\{C_8H_8(SiMe_3)\}]$. Crystals are triclinic, space group $P\bar{1}$, with $Z = 2$ in a unit cell of dimensions: $a = 9.972(3)$, $b = 16.082(6)$, $c = 6.662(2)$ Å, $\alpha = 89.46(2)$, $\beta = 110.44(2)$, and $\gamma = 82.46(2)°$. The structure has been determined by heavy-atom methods from diffractometer data and refined to *R* 0.035 for 3 146 independent reflections. The results establish that one $SiMe_3$ group is bonded to ruthenium and one to the C_8 ring. The hydrocarbon ligand is co-ordinated to the ruthenium through η^3-allyl and η^2-ethylenic interactions within a C_8 ring, with another ethylenic bond unco-ordinated. The complex exhibits fluxional behaviour in solution, which has been investigated by variable-temperature ^1H and ^{13}C n.m.r. spectroscopy. Heating cyclo-octatetraenes C_8H_7R with $[Ru(SiMe_3)_2(CO)_4]$ in heptane, or heating $[Ru(SiMe_3)(CO)_2\{C_8H_7R(SiMe_3)\}]$ directly in heptane or octane, effects ring closure with ejection of the *C*-bonded $SiMe_3$ group, producing diruthenium pentalene complexes $[Ru_2(SiMe_3)_2(CO)_4(C_8H_5R)]$ in moderate yield. Under mild conditions (hexane reflux) $[Ru(GeMe_3)_2(CO)_4]$ with cyclo-octatetraene yields small amounts of $[Ru(GeMe_3)(CO)_2\{C_8H_8(GeMe_3)\}]$ whereas $[Ru(SiMe_3)(GeMe_3)(CO)_4]$ readily gives $[Ru(GeMe_3)(CO)_2\{C_8H_8(SiMe_3)\}]$. In heptane or octane $[Ru(GeMe_3)_2(CO)_4]$ undergoes more complex reactions, affording $[Ru(GeMe_3)(CO)_2(C_8H_9)]$, $[Ru_2(GeMe_3)_2(CO)_4(C_8H_8)]$, and $[Ru_2(GeMe_3)_2(CO)_4(C_8H_6)]$. The mechanism of pentalene–ruthenium complex formation is discussed.

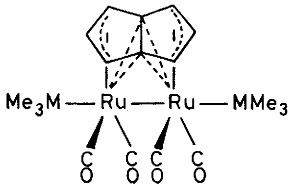
THE high reactivity of pentalene (1) precludes its isolation as a product from conventional organic syntheses but it can be stabilised as a ligand bridging two transition-metal atoms. We have recently reviewed[2] the various approaches employed in achieving the complexation of pentalene and its derivatives by metals. This paper is the first of three which describe our approach; namely, the dehydrogenative ring closure of cyclo-octatetraenes and cyclo-octatrienes induced by carbonylruthenium complexes. It is noteworthy that other routes require the use of organic precursors which already contain the relatively inaccessible bicyclic pentalene carbon skeleton. We describe herein the formation of diruthenium pentalene complexes in reactions of *cis*-$[Ru(MMe_3)(M'Me_3)(CO)_4]$ (2) with cyclo-octatetraenes C_8H_7R (R = H, Me, Ph, or $SiMe_3$). At the time $[Ru_2(GeMe_3)_2(CO)_4(C_8H_6)]$ (3b) was first reported[3] it represented the first example of a carbonylmetal complex of unsubstituted pentalene.



(1)



(2a) M = M' = Si
(2b) M = M' = Ge
(2c) M = Si, M' = Ge



(3a) M = Si
(3b) M = Ge

RESULTS AND DISCUSSION

The products of reaction of complexes (2) with cyclo-octatetraene (cot) or the monosubstituted cyclo-octatetraenes C_8H_7R (R = Me, Ph, or $SiMe_3$), depend markedly on the reaction temperature. In *hexane*, at reflux, complexes $[Ru(MMe_3)(CO)_2\{1\text{—}3:6\text{—}7\text{-}\eta\text{-}C_8H_8\text{-}(8\text{-}endo\text{-}MMe_3)\}]$ (4) are produced with cot, while in *heptane* the reaction yields the pentalene complexes $[Ru_2(MMe_3)_2(CO)_4(C_8H_6)]$ (3). With both solvents a competing ring closure is evident in the isolation of the known[4] tetrahydropentalenyl complexes $[Ru(MMe_3)(CO)_2(C_8H_9)]$ (5) as minor products. The monosubstituted cyclo-octatetraenes react analogously to yield the appropriate R-substituted derivatives of (3)—(5).

Heating (2a) with cot in *hexane* provides a high yield (*ca.* 80%) of white crystalline $[Ru(SiMe_3)(CO)_2\{1\text{—}3:6\text{—}7\text{-}\eta\text{-}C_8H_8(8\text{-}endo\text{-}SiMe_3)\}]$ (4a) after 24 h. Both ^1H and ^{13}C n.m.r. spectra, recorded at various temperatures, indicated that the product was fluxional (see below), that

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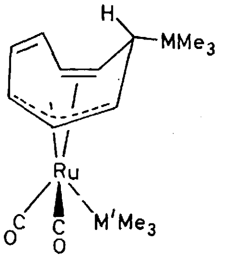
[1] Part 10, J. D. Edwards, S. A. R. Knox, and F. G. A. Stone, *J.C.S. Dalton*, 1976, 1813.

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

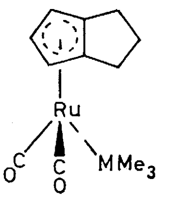
[3] A. Brookes, J. A. K. Howard, S. A. R. Knox, F. G. A. Stone, and P. Woodward, *J.C.S. Chem. Comm.*, 1973, 587.

[4] S. A. R. Knox, R. P. Phillips, and F. G. A. Stone, *J.C.S. Dalton*, 1974, 658.

an unusual hydrocarbon ligand was present, and that very probably one $SiMe_3$ ligand was *Ru*-bonded and one



(4a) M = M' = Si
(4b) M = M' = Ge
(4c) M = Si, M' = Ge



(5a) M = Si
(5b) M = Ge

C-bonded. Thus, the ^1H n.m.r. spectrum showed $SiMe_3$ group signals at τ 9.82 and 9.96, while the ^{13}C spectrum had corresponding signals 4.3 p.p.m. downfield and 4.3 p.p.m. upfield of $SiMe_4$. We have recently described [5,6]

TABLE 1

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

Atom	*x*	*y*	*z*
Ru	1.094 64(4)	0.199 13(2)	0.336 16(6)
Si(1)	1.350 3(2)	0.185 4(1)	0.540 9(3)
C(101)	1.465 9(10)	0.173 1(7)	0 367 8(18)
C(102)	1.400 3(10)	0.280 3(6)	0.696 7(18)
C(103)	1.416 1(10)	0.091 2(6)	0.737 4(16)
C(11)	1.148 2(6)	0.105 6(3)	0.199 6(8)
O(11)	1.179 1(6)	0.047 4(2)	0.117 5(7)
C(12)	1.136 3(6)	0.285 2(3)	0.179 7(8)
O(12)	1.163 7(6)	0.337 6(3)	0.091 1(7)
C(1)	0.837 3(6)	0.179 1(4)	0.137 4(9)
C(2)	0.839 7(5)	0.261 2(3)	0.186 7(8)
C(3)	0.839 1(5)	0.294 2(3)	0.397 6(8)
C(4)	0.996 0(5)	0.281 0(3)	0.546 2(7)
C(5)	1.069 6(6)	0.204 5(3)	0.650 4(7)
C(6)	1.040 6(6)	0.124 0(3)	0.573 1(8)
C(7)	0.894 6(7)	0.097 1(3)	0.471 6(1)
C(8)	0.808 8(7)	0.117 0(4)	0.274 4(12)
Si(3)	0.746 2(2)	0.406 2(1)	0.376 1(2)
C(31)	0.831 3(8)	0.477 2(4)	0.252 9(10)
C(32)	0.765 4(8)	0.436 0(4)	0.654 9(10)
C(33)	0.552 6(7)	0.409 0(4)	0.209 7(11)
H(1011)	1.552(11)	0.173(6)	0.455(16)
H(1012)	1.445(11)	0.130(6)	0.299(15)
H(1013)	1.435(9)	0.222(5)	0.245(12)
H(1021)	1.357(9)	0.292(5)	0.795(12)
H(1022)	1.481(8)	0.275(5)	0.763(12)
H(1023)	1.369(10)	0.325(5)	0.605(13)
H(1031)	1.383(9)	0.092(5)	0.854(12)
H(1032)	1.397(9)	0.044(5)	0.680(12)
H(1033)	1.501(9)	0.091(5)	0.804(13)
H(311)	0.925(7)	0.466(4)	0.298(10)
H(312)	0.825(7)	0.462(4)	0.122(9)
H(313)	0.809(7)	0.526(4)	0.277(10)
H(321)	0.846(7)	0.438(4)	0.715(10)
H(322)	0.724(9)	0.487(5)	0.666(12)
H(323)	0.715(6)	0.396(3)	0.709(9)
H(331)	0.541(6)	0.388(3)	0.063(9)
H(332)	0.518(8)	0.383(4)	0.286(10)
H(333)	0.506(8)	0.467(4)	0.198(10)
H(1)	0.824(6)	0.166(3)	0.999(9)
H(2)	0.853(5)	0.300(3)	0.093(7)
H(3)	0.797(5)	0.265(2)	0.447(6)
H(4)	1.030(5)	0.326(3)	0.610(7)
H(5)	1.160(5)	0.208(3)	0.764(7)
H(6)	1.108(5)	0.079(3)	0.659(7)
H(7)	0.872(6)	0.068(3)	0.549(8)
H(8)	0.720(6)	0.091(3)	0.220(9)

TABLE 2

Bond lengths (Å) and angles (°) for complex (4a)

(*a*) Distances

(*i*) $Ru(SiMe_3)(CO)_2$ group

Ru–Si(1)	2.414(2)	C(102)–H(1023)	0.89(8)
Si(1)–C(101)	1.891(13)	C(103)–H(1031)	0.95(10)
Si(1)–C(102)	1.877(11)	C(103)–H(1032)	0.87(8)
Si(1)–C(103)	1.882(10)	C(103)–H(1033)	0.81(8)
C(101)–H(1011)	0.85(10)	Ru–C(11)	1.895(5)
C(101)–H(1012)	0.84(9)	C(11)–O(11)	1.135(7)
C(101)–H(1013)	1.06(7)	Ru–C(12)	1.897(6)
C(102)–H(1021)	0.91(10)	C(12)–O(12)	1.139(8)
C(102)–H(1022)	0.76(7)		

(*ii*) $C_8H_8(SiMe_3)$ ring

C(1)–C(2)	1.365(8)	C(31)–H(311)	0.87(7)
C(2)–C(3)	1.508(8)	C(31)–H(312)	0.89(6)
C(3)–C(4)	1.516(6)	C(31)–H(313)	0.82(6)
C(4)–C(5)	1.387(6)	C(32)–H(321)	0.77(6)
C(5)–C(6)	1.425(7)	C(32)–H(322)	0.89(8)
C(6)–C(7)	1.499(9)	C(32)–H(323)	1.00(7)
C(7)–C(8)	1.302(9)	C(33)–H(331)	1.01(6)
C(8)–C(1)	1.466(10)	C(33)–H(332)	0.84(8)
Ru–C(1)	2.509(6)	C(33)–H(333)	0.97(6)
Ru–C(2)	2.449(5)	C(1)–H(1)	0.91(6)
Ru–C(3)	2.952(5)	C(2)–H(2)	0.93(5)
Ru–C(4)	2.305(5)	C(3)–H(3)	0.81(5)
Ru–C(5)	2.195(5)	C(4)–H(4)	0.88(5)
Ru–C(6)	2.229(6)	C(5)–H(5)	0.96(4)
C(3)–Si(3)	1.894(5)	C(6)–H(6)	0.95(4)
Si(3)–C(31)	1.850(8)	C(7)–H(7)	0.80(6)
Si(3)–C(32)	1.873(7)	C(8)–H(8)	0.98(6)
Si(3)–C(33)	1.854(6)		

(*b*) Angles

Ru–Si(1)–C(101)	113.1(3)	C(4)–C(5)–C(6)	125.3(4)
Ru–Si(1)–C(102)	112.1(3)	C(5)–C(6)–C(7)	126.6(5)
Ru–Si(1)–C(103)	112.9(3)	C(6)–C(7)–C(8)	124.9(7)
C(101)–Si(1)–C(102)	105.4(5)	C(7)–C(8)–C(1)	122.2(6)
C(102)–Si(1)–C(103)	107.4(5)	C(8)–C(1)–C(2)	121.5(6)
C(103)–Si(1)–C(101)	105.4(5)	C(2)–C(3)–Si(3)	114.2(3)
Si(1)–Ru–C(11)	84.2(2)	C(4)–C(3)–Si(3)	113.9(3)
Si(1)–Ru–C(12)	83.3(2)	C(3)–Si(3)–C(31)	110.2(3)
C(11)–Ru–C(12)	98.6(3)	C(3)–Si(3)–C(32)	107.2(2)
Ru–C(11)–O(11)	177.0(6)	C(3)–Si(3)–C(33)	108.2(2)
Ru–C(12)–O(12)	178.0(6)	C(31)–Si(3)–C(32)	110.5(3)
C(1)–C(2)–C(3)	124.7(5)	C(32)–Si(3)–C(33)	110.3(4)
C(2)–C(3)–C(4)	105.6(4)	C(33)–Si(3)–C(31)	110.4(3)
C(3)–C(4)–C(5)	124.1(4)		

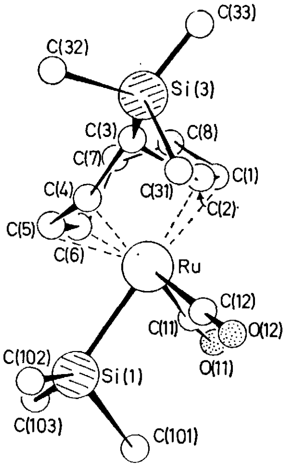


FIGURE 1 Molecular structure of $[Ru(SiMe_3)(CO)_2\{C_8H_8(SiMe_3)\}]$ (4a)

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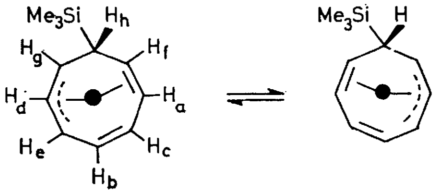
[5] A. Brookes, S. A. R. Knox, V. Riera, B. A. Sosinsky, and F. G. A. Stone, *J.C.S. Dalton*, 1975, 1641.

[6] S. A. R. Knox, B. A. Sosinsky, and F. G. A. Stone, *J.C.S. Dalton*, 1975, 1647.

other complexes containing two such $SiMe_3$ groups, and their n.m.r. spectra exhibit the same features. The formulation (4a) was unequivocally established by an *X*-ray diffraction study.

The overall configuration of the molecule and the atom-numbering system are shown in Figure 1, while Tables 1 and 2 summarise the crystallographic results. The C_8 ring is η^5-bonded to the ruthenium atom *via* an η^2-olefinic interaction of C(1) and C(2) and an η^3-allyl system C(4)—C(6). The double bond between C(7) and C(8) is unco-ordinated, while carbon atom C(3) carries a trimethylsilyl group in an *endo* orientation with respect to the metal. As has been observed elsewhere,[7] the trimethylsilyl group attached to the metal atom is of significantly different geometry from that of the $SiMe_3$ group on the C_8 ring. The Ru–Si(1) bond length (2.414 Å) is notably short (the analogous Ru–Si distance in $[Ru_2(SiMe_3)(CO)_5\{C_7H_6(SiMe_3)\}]$ [7] is 2.452 Å, while the sum of the covalent radii is 2.59 Å), and the C–Si(1)–C angles are all less than the ideal tetrahedral value. The ring $SiMe_3$ group, on the other hand, is normal in its bond lengths and its angles. The carbonyls and $SiMe_3$ group on the ruthenium are approximately orthogonal.

Because of the space-group symmetry ($P\bar{1}$) the crystal contains equal numbers of the two enantiomorphous forms of the complex. Moreover, it is clear, in the light of the structural determination, that the ^1H and ^{13}C n.m.r. spectra described below are compatible with a fluxional interconversion of these enantiomorphs in solution, as shown in Scheme 1.



● = $Ru(SiMe_3)(CO)_2$

SCHEME 1

Figure 2 shows the ^1H n.m.r. spectrum of (4a) between −60 and 70 °C. Over the entire temperature range the two trimethylsilyl signals remain unchanged and need not be considered further. At the low-temperature limit the eight ring protons appear as eight distinct, nearly first-order, signals in accord with the structure in the solid established by *X*-ray diffraction, while the changes which occur on warming demand the generation of a time-averaged mirror plane of molecular symmetry. Only the oscillation in bonding represented in Scheme 1 can provide such a mirror plane, and it is important to note that the two protons (*b* and *h* of Figure 2) which maintain their chemical shift between −60 and 70 °C must lie on this mirror plane. The assignment of signal *h* to the *exo* aliphatic hydrogen of the ring and *b* to the indicated olefinic hydrogen is made readily on the basis of their respective shifts.

Assignment of the remaining six ring protons of the hydrocarbon ligand was achieved by double-irradiation experiments performed at −60 °C, which indicated a coupling pattern $\overline{a\text{–}c\text{–}b\text{–}e\text{–}d\text{–}g\text{–}h\text{–}f}$. Since *b* and *h* are identified, and signal *c* is more reasonably due to an unco-ordinated olefinic proton than is signal *e*, the total assignment of the static molecule is made as in the Scheme. This assignment requires a large chemical-shift difference between protons *a* and *f* of the co-ordinated double bond, *a* in fact being at lowest field

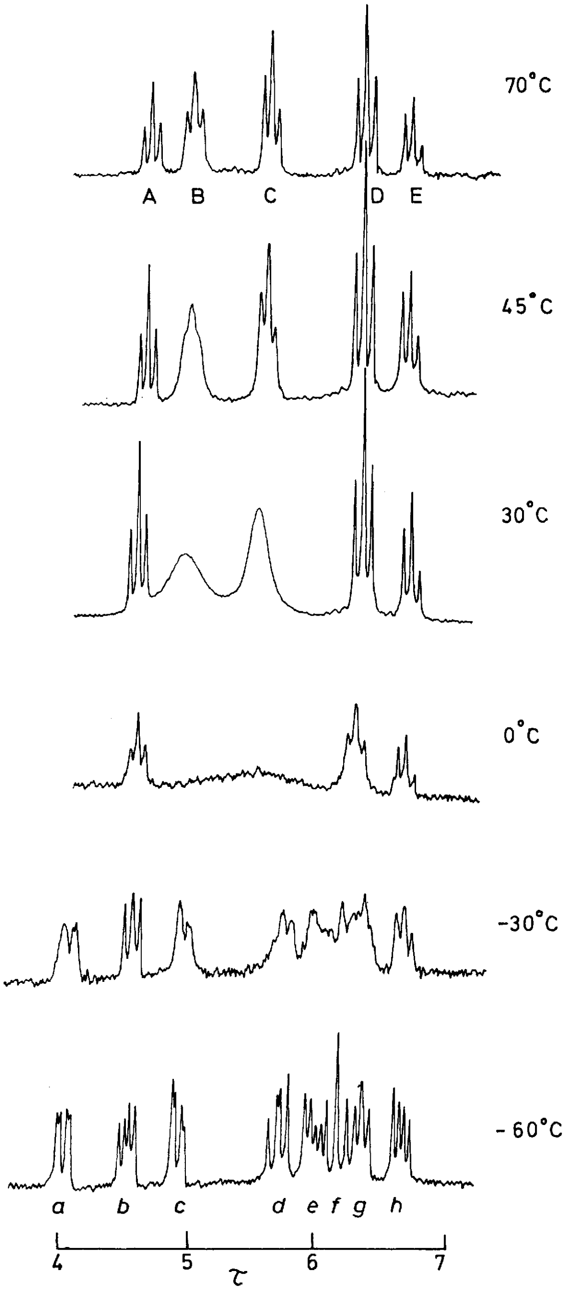


FIGURE 2 Hydrogen-1 n.m.r. spectrum of $[Ru(SiMe_3)(CO)_2\text{-}\{C_8H_8(SiMe_3)\}]$ (4a) in octane (30—70 °C) and in CF_2Cl_2–CF_2ClH (1 : 1) (0 to −60 °C) solution

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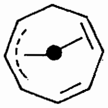
[7] J. A. K. Howard and P. Woodward, *J.C.S. Dalton*, 1975, 59.

(τ 4.02) of all the ring protons. There is good precedence for this, however, in the suggestion [8] that the similarly bonded [Ru(CO)$_3$(1—3 : 6—7-η-C$_8$H$_9$)][BF$_4$] (6a) has the proton corresponding to *a* also at very low field (τ 3.52) for one of co-ordinated olefinic character.



(6a) ● = Ru(CO)$_3^+$BF$_4^-$
(6b) ● = Co(η^4-C$_8$H$_8$)

As required by Scheme 1, and in confirmation of the above assignments, on warming there is pairwise averaging of environments *a–d*, *c–e*, and *f–g*, so that the high-temperature limiting spectrum comprises five signals (A—E) in the intensity ratio 1 : 2 : 2 : 2 : 1. Taking the mean values of the chemical shifts of *a* and *d* (τ 4.95), *c* and *e* (5.50), and *f* and *g* (6.36) clearly establishes the origins of the signals B (τ 4.94), C (5.52), and D (6.39). Signals A—E also show the results of averaging the coupling of the ring protons with their neighbours by the fluxional oscillation.

The chemical-shift separations of the protons *a* and *d* (175), *c* and *e* (110), and *f* and *g* (20 Hz), which are averaged by the fluxional oscillation, and their corresponding coalescence temperatures (273, 265, and 248 K respectively), allow three-fold calculation [9] of the free energy of activation of the process, providing a value of 12.6 ± 0.2 kcal mol^{-1}.*

The ^{13}C n.m.r. spectrum of (4a) in CDCl$_3$ between −30 and 50 °C varies in a manner completely consistent with the proposed dynamic process. At −30 °C a limiting low-temperature spectrum is observed, with eight ring-carbon signals at 19.4, 40.2, 67.0, 71.8, 102.7, 115.6, 125.1, and 131.4 p.p.m. downfield of SiMe$_4$. There are two SiMe$_3$ group signals, 4.3 p.p.m. downfield (Ru–SiMe$_3$) and 4.3 p.p.m. upfield (C–SiMe$_3$) of SiMe$_4$, which are temperature invariant. The ring-carbon signals at highest and lowest field remain sharp on warming to 50 °C, and are evidently due to the two carbons which lie on the time-averaged mirror plane. The other six ring-carbon resonances collapse, becoming lost in the noise level at 0 °C, and by 50 °C are still not fully averaged. At this temperature a quite sharp signal has appeared at 109.2 p.p.m., and a broad weak one centred at *ca.* 57 p.p.m. The former is at exactly the mean shift value of two low-temperature signals (115.6 and 102.7 p.p.m.) and the other very near to the mean (56.0 p.p.m.) of two others (71.8 and 40.2 p.p.m.). The third pair of carbons remains unaveraged and obscured by noise even at 50 °C, as befits its greater shift separation (58.1 p.p.m.) when compared with the other pairs (12.9 and 31.6 p.p.m.). Efforts to obtain a limiting high-temperature spectrum above 50 °C were foiled by significant decomposition of the complex at elevated temperatures (see description of experiments on thermal decomposition below).

It is of interest that the i.r. spectrum of (4a) exhibits a band at 1 643 cm^{-1} attributable to a stretching mode of a free double bond. Complexes such as [Fe(CO)$_3$(η^4-C$_8$H$_8$)] and [Ru(η^4-C$_8$H$_8$)(η-C$_6$H$_6$)],[10a] in which the metal utilises all the double bonds of cyclo-octatetraene during a succession of 1,2 shifts about the ring, show related absorptions at much lower energy (1 562 and 1 530 cm^{-1} respectively). This difference may be significant in indicating that the unco-ordinated olefinic bond of (4a) does not at any time become co-ordinated during the fluxional oscillation.

Other cyclo-octatrienyl complexes are known which involve a co-ordination of a C$_8$ ring to a transition metal analogous to that determined for (4a). Complex (6a) [8] has already been mentioned; another example is provided by [Co(η^4-C$_8$H$_8$)(1—3 : 6—7-η-C$_8$H$_9$)] (6b).[10b,11] Although in principle the same fluxional process observed for (4a) is possible for each complex (6), only for (6b) does it occur.[11]

The germanium complex (4b) is formed in detectable quantities only after several weeks' reflux of cot with (2b) in *hexane*. Reaction of (2c) with cot in hexane, however, proceeded more readily, affording [Ru(GeMe$_3$)(CO)$_2${1—3 : 6—7-η-C$_8$H$_8$(8-*endo*-SiMe$_3$)}] (4c) in 50% yield after 48 h. The ^{1}H n.m.r. spectra (Table 3) of both (4b) and (4c) at room temperature are very similar to that of (4a), indicating comparable fluxional behaviour. On cooling (4c) to −60 °C analogous changes do in fact occur to give a limiting low-temperature spectrum like that of (4a).

We take the *endo* position for the ring MMe$_3$ group relative to the metal in the complexes (4) to imply an intramolecular migration of the group from ruthenium to co-ordinated hydrocarbon, perhaps within a complex of the type [Ru(MMe$_3$)$_2$(CO)$_2$(η^4-C$_8$H$_8$)]. The reaction of complexes (2) with a cyclic polyolefin to yield a five-electron hydrocarbon ligand containing a migrated MMe$_3$ group is apparently general. That with cot here described must be added to those with cycloheptatriene [5] and azulene [6] reported previously, which provide complexes (7) and (8) respectively. As seen above, the product of the reaction of cot with [Ru(SiMe$_3$)(GeMe$_3$)(CO)$_4$] (2c) clearly illustrates a preference for SiMe$_3$ rather than GeMe$_3$ migration from ruthenium to this hydrocarbon. This same preference is manifested in the reactions of (2c) with cycloheptatriene and azulene, but not as exclusively as here. Somewhat surprisingly, in this light, the reaction of (2a) with cot occurs more smoothly and in higher yield when compared with (2b), whereas for cycloheptatriene and azulene the converse holds.

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* Throughout this paper: 1 cal = 4.184 J; 1 mmHg ≈ 13.6 × 9.8 Pa.

[8] M. Cooke, P. T. Draggett, M. Green, B. F. G. Johnson, J. Lewis, and D. J. Yarrow, *Chem. Comm.*, 1971, 621.

[9] D. Kost, E. H. Carlson, and M. Raban, *Chem. Comm.*, 1971, 656.

[10] (*a*) R. T. Bailey, E. R. Lippincott, and D. Steele, *J. Amer. Chem. Soc.*, 1965, **87**, 5346; (*b*) A. Greco, M. Green, and F. G. A. Stone, *J. Chem. Soc.* (*A*), 1971, 285.

[11] P. V. Rinze, *J. Organometallic Chem.*, 1975, **90**, 343.

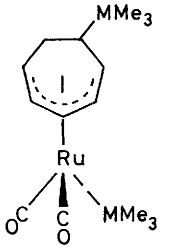
TABLE 3

Spectroscopic properties of the new complexes

Complex	ν(CO) [a]/cm^{-1}	^{1}H N.m.r. (τ) [b]
$[Ru_2(SiMe_3)_2(CO)_4(C_8H_6)]$ (3a)	2 032s, 2 025w, 1 997w, 1 979s	4.34 (2 H, t, *J* 2.5), 6.54 (4 H, d, *J* 2.5), 9.60 (18 H, s)
$[Ru_2(GeMe_3)_2(CO)_4(C_8H_6)]$ (3b)	2 029s, 2 023w, 1 995w, 1 977s	4.24 (2 H, t, *J* 2.5), 6.50 (4 H, d, *J* 2.5), 9.40 (18 H, s)
$[Ru(SiMe_3)(CO)_2\{C_8H_8(SiMe_3)\}]$ (4a)	2 012s, 1 956s	[c] 4.54 (1 H, t, *J* 6.5), 4.94 (2 H, br), 5.52 (2 H, br), 6.39 (2 H, t, *J* 7.0), 6.79 (1 H, t, *J* 6.5) 9.82 (9 H, s), 9.96 (9 H, s)
$[Ru(GeMe_3)(CO)_2\{C_8H_8(GeMe_3)\}]$ (4b)	2 011s, 1 955s	4.59 (1 H, t, *J* 6.5), 5.00 (2 H, br), 5.59 (2 H, br), 6.49 (3 H, m), 9.71 (9 H, s), 9.82 (9 H, s)
$[Ru(GeMe_3)(CO)_2\{C_8H_8(SiMe_3)\}]$ (4c)	2 010s, 1 958s	4.50 (1 H, t, *J* 6.5). 4.90 (2 H, br), 5.46 (2 H, br), 6.34 (2 H, m), 6.72 (1 H, m), 9.80 (9 H, s), 9.95 (9 H, s)
$[Ru(SiMe_3)(CO)_2\{C_8H_7(SiMe_3)_2\}]$ (9a)	2 010s, 1 956s	3.79 (1 H, d, *J* 8), 4.39 (1 H, d, *J* 4), 5.80 (2 H, m), 6.32 (1 H, t, *J* 8), 6.44 (1 H, m), 7.13 (1 H, dd, *J* 5.8), 9.80 (9 H, s), 9.94 (9 H, s), 9.96 (9 H, s)
$[Ru(SiMe_3)(CO)_2\{C_8H_7Me(SiMe_3)\}]$ (9b)	2 011s, 1 957s	4.20 (1 H, m), 5.07 (1 H, m), 5.81 (1 H, dd, *J* 7,8), 6.0—6.5 (3 H, m), 6.83 (1 H, dd, *J* 6, 7), 8.26 (3 H, s), 9.72 (9 H, s), 9.97 (9 H, s)
$[Ru_2(SiMe_3)_2(CO)_4\{C_8H_5(SiMe_3)\}]$ (14a)	2 031s, 2 025w, 1 997w, 1 980s	4.14 (1 H, t, *J* 2.5), 4.22 (1 H, d, *J* 2.5), 6.31 (1 H, d, *J* 2.5), 6.48 (1 H, d, *J* 2.5), 6.58 (1 H, d, *J* 2.5), 9.64 (18 H, s), 9.90 (9 H, s)
$[Ru_2(SiMe_3)_2(CO)_4(C_8H_5Me)]$ (14b)	2 031s, 1 995w, 1 977s	[d] 4.37 (1 H, s, br), 4.46 (1 H, s, br), 6.57 (1 H, s, br), 9.62 (9 H, s), 6.66 (1 H, s, br), 6.87 (1 H, s, br), 8.50 (3 H, s), 9.60 (9 H, s), 9.62 (9 H, s)
$[Ru_2(SiMe_3)_2(CO)_4(C_8H_5Ph)]$ (14c)	2 030s, 1 993w, 1 976s	[e] 2.50 (5 H, m), 3.82 (1 H, d, *J* 2), 4.20 (1 H, dd, *J* 2, 3), 6.23 (1 H, d, *J* 2), 6.47 (1 H, d, *J* 3), 6.60 (1 H, d, *J* 2), 9.48 (9 H, s), 9.65 (9 H, s)

[a] In hexane solution. [b] In $CDCl_3$ solution; *J* in Hz. [c] In CCl_4 solution. [d] Broadness due to unresolved coupling. [e] In CCl_3F solution.

The reactions of (2a) with the substituted cyclooctatetraenes C_8H_7R (R = Me, Ph, or $SiMe_3$) in *hexane* proceed as for cot itself to afford the migration products $[Ru(SiMe_3)(CO)_2\{C_8H_7(R)(SiMe_3)\}]$ (9) in good to excellent yield, in addition to an R-substituted derivative of (5a) in low yield. Complex (9c) could not be cleanly separated from the co-product, but pure samples of (9a) and (9b) were readily obtained. The ^1H n.m.r. spectra (Table 3) of the complexes $[Ru(SiMe_3)(CO)_2\{C_8H_7(R)(SiMe_3)\}]$ reveal that migration of the $SiMe_3$ group occurs with high specificity, in that for R = $SiMe_3$ exclusive formation of the isomer (9a) is indicated while, for R = Me, (9b) appears to be a highly dominant component of an isomeric mixture. In addition to the signals reported in Table 3, (9b) has weak methyl (τ 7.90, 8.46, and 8.63) and $SiMe_3$ group (τ 10.03) signals due to the presence of other isomers. The spectra of (9a) and (9b) are temperature invariant between −60 and 60 °C and very similar to that of (4a) at −60 °C; *i.e.* the introduction of an extra substituent into the C_8 ring of (4a) has removed the fluxionality. Comparison of the n.m.r. spectra of (9a) and of (9b) with that of (4a) provides strong evidence for the structure assigned, in that the resonance due to proton *c* of (4a) (see Scheme 1) is not present in (9a) or (9b). Moreover, a 220-MHz ^1H spectrum of (9a) showed that the signals corresponding to protons *a* and *b* of (4a) are reduced to doublets, confirming that substitution occurs between these two sites. Clearly, only if substitution occurred in place of proton *b* of (4a) could fluxionality be retained. In any other position an oscillation, as in Scheme 1, generates an isomer rather than an equivalent species of equal free energy. Although in principle such a non-degenerate interconversion could occur, the barrier is evidently too high for its observation at 60 °C.



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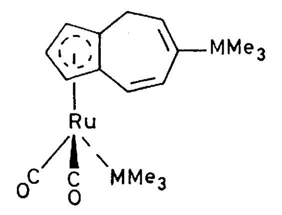

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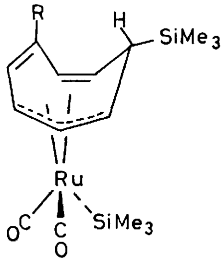
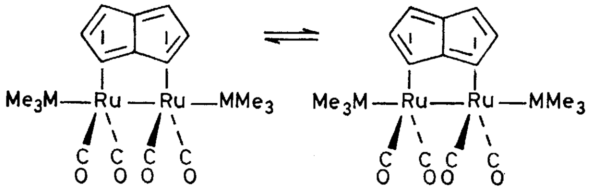


(9a) R = $SiMe_3$
(9b) R = Me
(9c) R = Ph

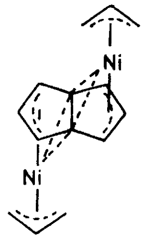
Treatment of (2a) with cot in *heptane* at reflux generates the air-, solution-, and thermally-stable colourless crystalline pentalene complex $[Ru_2(SiMe_3)_2(CO)_4(C_8H_6)]$ (3a) in 33% yield, together with a small amount of (5a). The corresponding reaction with (2b) is less clean, affording several other products in addition to (5b) and an 11% yield of the pale yellow crystalline pentalene complex $[Ru_2(GeMe_3)_2(CO)_4(C_8H_6)]$ (3b).

The ^1H n.m.r. spectra (Table 3) of complexes (3) strongly indicated the presence of pentalene as a ligand; *e.g.* for (3a) there are two signals due to the hydrocarbon ligand, one a triplet [τ 4.3 (*J* 2.5 Hz)] and the other a doublet [τ 6.5 (J 2.5 Hz)] of relative intensity 2 : 4. This was firmly established by an *X*-ray diffraction study of (3b), which is reported in detail in the following paper.[12]

The distinctive features of the structure are a near-linear (Ge–Ru–Ru 171°) metal-atom sequence, symmetrically bonded through the two ruthenium atoms to a pentalene which has its two component five-membered rings hinged at an angle of 173° away from the molecular centre. The Ru–C (ring) distances indicate the bonding scheme in (3). Each ruthenium is envisaged as bonded to an interannular η^3-allyl unit, the relevant carbons being 2.21 Å distant on average, while two 'bridging' carbons (equivalent, at 2.53 Å, from each ruthenium) are involved in a four-electron four-centre (2Ru–2C) interaction. Such 'bridging' carbons have been invoked for the tetramethylcyclo-octatetraene complex [$Fe_2(CO)_5(C_8H_4Me_4)$],[13] and occur in several other polyolefin transition-metal complexes.[14]



(10a) (10b)



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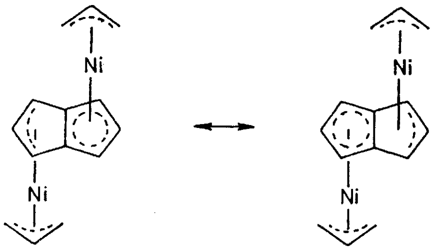
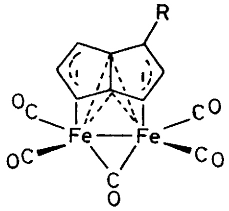


(11a) (11b)



(12)

Pentalene is predicted[15] to have a substantially localised polyolefin ground-state structure (1). Any possibility, however, that complexes (3) might be fluxional in the sense (10a) ⇌ (10b) is negated both by the *X*-ray diffraction determination of the ground-state structure and by the observed invariance of the n.m.r. spectra between 30 and −100 °C. One other dimetal complex of pentalene has been the subject of an *X*-ray diffraction study. In contrast to (3), the complex [$Ni_2(\eta\text{-}C_3H_5)_2(C_8H_6)$] (11)[16,17] has the metal atoms on opposite sides of a planar pentalene ligand, but can also, on the basis of the Ni–C(ring) distances, be represented in an η^3-allyl–'bridging-carbon' mode. Although diamagnetic, (11) is two electrons short of satisfying the 18-electron rule, as is best seen from the valence-bond representation (11a) ↔ (11b).

Of several attempts to synthesise complexes of pentalene from the reaction of the aromatic 10 π-electron pentalene dianion with metal halides, that of (11) from [$Ni_2Cl_2(\eta\text{-}C_3H_5)_2$] and $K_2C_8H_6$ is the only authenticated success. The complexes [$Co_2(C_8H_6)_2$][18] and [$Ni_2(C_8H_6)_2$][19] have been similarly prepared, but their nature is as yet undetermined. Carbonyliron complexes [$Fe_2(CO)_5(C_8H_5R)$] (12; R = H, Ph, or NMe_2) have been obtained from the reaction of iron carbonyls with the appropriate dihydropentalene[20] or the dimer of pentalene,[21] and it seems likely that the pentalene ligand is co-ordinated to the di-iron unit as shown, comparable to that in (3).

The reaction of (2b) with cot in *heptane* also yields (9%) a complex formulated as [$Ru_2(GeMe_3)_2(CO)_4(C_8H_8)$] (13), structurally closely related to (3). This complex, its silicon analogue, and ring-substituted derivatives are much better obtained by treating the binuclear ruthenium complexes [$Ru_2(MMe_3)_2(CO)_8$] with cyclo-octatetraenes and will be discussed in detail in a forth-

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[12] J. A. K. Howard and P. Woodward, *J.C.S. Dalton*, following paper.

[13] F. A. Cotton and M. D. LaPrade, *J. Amer. Chem. Soc.*, 1968, **90**, 2026.

[14] 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 and refs. therein.

[15] N. C. Baird and R. M. West, *J. Amer. Chem. Soc.*, 1971, **93**, 3072.

[16] A. Miyake and A. Kanai, *Angew. Chem. Internat. Edn.*, 1971, **10**, 801.

[17] Y. Kitano, M. Kashiwagi, and Y. Kinoshita, *Bull. Chem. Soc. Japan*, 1973, **46**, 723.

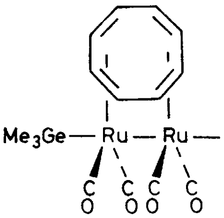
[18] T. J. Katz, N. Acton, and J. McGinnes, *J. Amer. Chem. Soc.*, 1972, **94**, 6205.

[19] T. J. Katz and N. Acton, *J. Amer. Chem. Soc.*, 1972, **94**, 3281.

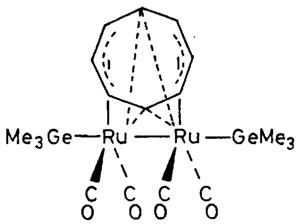
[20] D. F. Hunt and J. W. Russell, *J. Amer. Chem. Soc.*, 1972, **94**, 7198; *J. Organometallic Chem.*, 1972, **46**, C22.

[21] W. Weidemüller and K. Hafner, *Angew. Chem. Internat. Edn.*, 1973, **12**, 925.

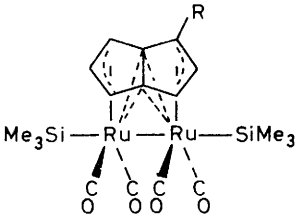
coming publication. The cot ligand of (13) is fluxional at all the accessible temperatures, and an *X*-ray diffraction study would be necessary to determine whether the ground-state structure is (13a) or (13b).



(13a)

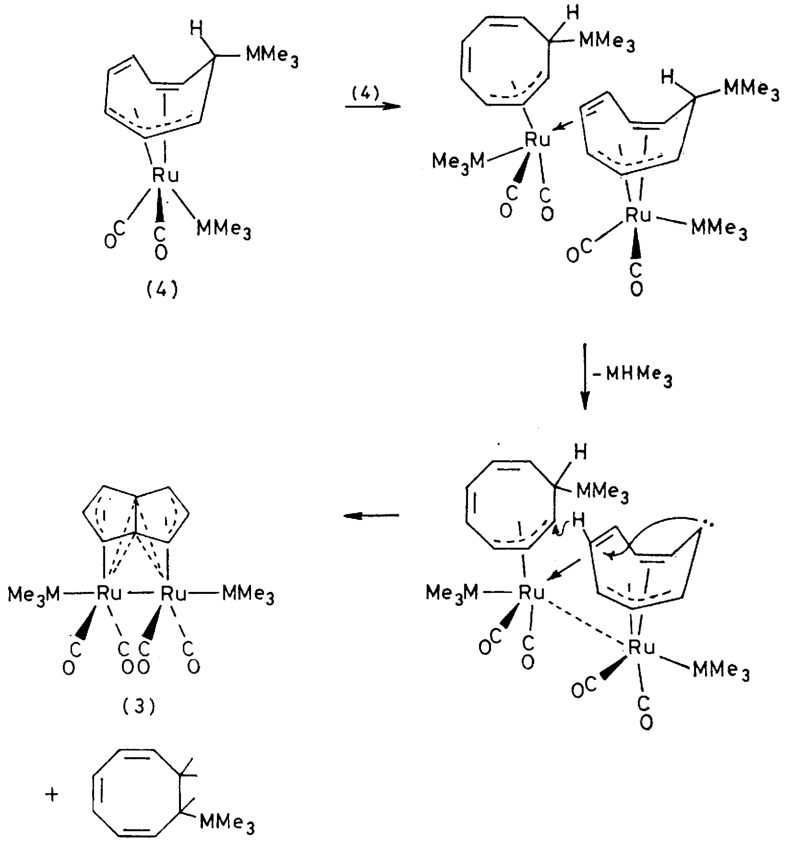


(13b)



(14a) R = $SiMe_3$
(14b) R = Me
(14c) R = Ph

Formation of pentalene complexes also occurs on heating (2) with substituted cyclo-octatetraenes at elevated temperatures. In *octane*, (2a) and phenylcyclo-octatetraene give an 11% yield of $[Ru_2(SiMe_3)_2(CO)_4(C_8H_5Ph\text{-}1)]$ (14c) in 17 h, a specificity of isomer formation also noted for methyl and $SiMe_3$ substitution (see below).



Scheme 2

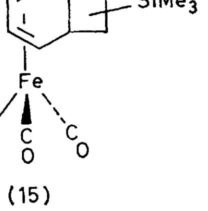
The formation of complexes (4) on heating (2) with cot in *hexane*, and of complexes (3) on heating the same reactants in *heptane*, suggests an intermediacy of (4) in the path leading to (3). This has been clearly established by studies on the thermolysis of complexes (4). Thus heating (4a) in octane for 2 h resulted in the formation of (3a) in 37% yield and a trace amount of (5a). Similarly, heating of (9a) or (9b) for 4—5 h provided again only trace amounts of ring-substituted derivatives of (5a), with the pentalene complexes (14a) and (14b) formed in 20—25% yield. The formulation of the pentalene complexes (14) as the 1-substituted isomers is clearly drawn from their ^1H n.m.r. spectra (see Table 3) which reveal an asymmetry in the C_8H_5R ligands incompatible with 2-substitution.

We suggest that the conversion of complexes (4) into the pentalene complexes (3) may proceed by the path summarised in Scheme 2. It is envisaged that the unco-ordinated double bond of (4) is the agent of attack on another molecule of (4) at ruthenium, effecting partial release of the hydrocarbon bonded to that metal atom.

There now must follow the release of one $C_8H_8(MMe_3)$ ligand while two hydrogen atoms and one MMe_3 group are lost from the other. In the Scheme we suggest this occurs *via* the generation of a ring carbene carbon by release of a molecule of $MHMe_3$ through an α-hydrogen elimination. Attack across the ring by this carbene carbon results in ring closure and formation of the pentalene skeleton. In effecting this transformation a hydrogen must be lost from the attacked carbon. This might either be released as a radical or transferred to the other C_8 ring, which would be ejected from complexation as the substituted cyclo-octatriene $C_8H_9(MMe_3)$. Simultaneous metal–metal bond formation and co-ordination of each ruthenium to the ring-closed ligand completes the process.

Although such a path is at first sight very speculative, there are several factors which support its proposal. First, no other reasonable initiation of the process than unco-ordinated olefinic bond attack on ruthenium is apparent. Further, the observation of a strong i.r. absorption at 2 120 cm^{-1} [typical of ν(SiH)] during the thermolysis of (4a), and its disappearance on placing the solution under reduced pressure, argues for the release of volatile $SiHMe_3$. Moreover, there is precedent for an $SiMe_3$ group inducing α-elimination and carbene formation, in a study of the decomposition of $CHF_2CF_2SiMe_3$.[22] It is also striking that the C(3)–C(7) distance (Figure 1) of 3.198 Å within (4a) is relatively short, the shortest of the 1,5-*trans*-annular distances, and compatible with ring closure linking these carbons. Finally, and compellingly, such ring closure accounts also for the exclusive formation of the 1-substituted pentalene complexes (14a) and (14b) on thermolysis of (9a) and (9b).

The postulated ejection of trimethylsilylcyclo-octatriene was investigated by adding $[Fe_2(CO)_9]$ to a solution resulting from thermolysis of (4a), in the expectation that the carbonyl would ' trap ' the triene as a tricarbonyliron complex. A complex of formulation $[Fe(CO)_3\{C_8H_9(SiMe_3)\}]$ was so isolated, identified by i.r. and mass spectra, but it is not clear from the ^{1}H n.m.r. spectrum how the hydrocarbon is co-ordinated to the metal. The spectrum is inconsistent with the expected formulation (15).



(15)

In conclusion, therefore, this work describes an intramolecular migration of a MMe_3 ligand from ruthenium to co-ordinated cyclo-octatetraene on reaction of the polyolefin with complexes $[Ru(MMe_3)_2(CO)_4]$, yielding $[Ru(MMe_3)(CO)_2\{C_8H_8(MMe_3)\}]$ which is thermally unstable with respect to ejection of the migrant MMe_3 group and ring closure to produce a pentalene ligand. Migration is shown to be more ready for $SiMe_3$ than $GeMe_3$, and to be specifically directed by ring substituents. Ring closure is likewise specific, in accord with the proposed path.

EXPERIMENTAL

Synthetic Studies.—Instrumentation and general experimental techniques were as described in previous papers in this series. Chromatography was performed on 50-cm columns, packed with alumina unless otherwise stated, using hexane or dichloromethane–hexane mixtures as eluant. Trimethylsilyl-,[23] phenyl-,[24] and methyl-cyclo-octatetraenes [25] were prepared by literature methods, as was $[Ru(GeMe_3)_2(CO)_4]$.[26] The complex $[Ru(SiMe_3)(GeMe_3)(CO)_4]$ was prepared in good yield by the method described in the literature for $[Ru(SiMe_3)(GeBu_3)(CO)_4]$.[27]

Preparation of $[Ru(SiMe_3)_2(CO)_4]$.—The literature method [27] (<10% yield) was modified as follows: $SiHMe_3$ (47.5 g, 642 mmol) was condensed (−196 °C) into a Hoke cylinder (*ca.* 150 cm^3 capacity) containing $[Ru_3(CO)_{12}]$ (8.8 g, 13.8 mmol) in hexane (50 cm^3). This was heated at 80 °C for 1 week, with periodic bleeding of hydrogen after temporary cooling to −196 °C. Solvent was removed, and the yellow liquid product distilled (80 °C, 10^{-1} mmHg) from the residue in 46% yield (6.85 g, 19.1 mmol), leaving yellow crystalline $[\{Ru(SiMe_3)(CO)_4\}_2]$ (3.1 g, 26%).

Reactions of $[Ru(MMe_3)_2(CO)_4]$ (2) *with Cyclo-octatetraene*—(*a*) $[Ru(SiMe_3)_2(CO)_4]$ (2a). (*i*) Complex (2a) (2.6 g, 7.2 mmol) and cot (7 cm^3, 60 mmol) were heated in hexane (25 cm^3) at reflux for 24 h. Solvent and excess of cot were removed *in vacuo*; chromatography then gave, in order of elution: a very pale yellow oil which crystallised from hexane at −78 °C as white *crystals* of $[Ru(SiMe_3)(CO)_2\{C_8H_8(SiMe_3)\}]$ (4a) (2.4 g, 82%) (Found: C, 47.0; H, 6.3; Ru, 24.7; Si, 13.9%, *M* 408. Calc. for $C_{16}H_{26}O_2RuSi_2$: C, 47.0; H, 6.4; Ru, 25.0; Si, 13.7%; *M* 408), m.p. 78 °C; followed closely by a small amount of a white oil $[Ru(SiMe_3)(CO)_2(C_8H_9)]$ (5a), identified by i.r. and mass spectra.[4]

(*ii*) After heating (18 h) cot (0.4 g, 4 mmol) and (2a) (0.2 g, 0.6 mmol) in *heptane* (50 cm^3) at reflux, chromatography on Florisil gave a small amount of (5a), followed by white *crystals* of $[Ru_2(SiMe_3)_2(CO)_4(C_8H_6)]$ (3a) (0.05 g, 33%) (Found: C, 37.5; H, 4.4%; *M* 563. Calc. for $C_{18}H_{24}O_4Ru_2Si_2$: C, 38.4; H, 4.3%; *M* 563), m.p. 221 °C (decomp.).

(*b*) $[Ru(GeMe_3)_2(CO)_4]$ (2b). (*i*) Complex (2b) (1.5 g, 3.3 mmol) and cot (1.0 g, 9.7 mmol) were heated in heptane (50 cm^3) at reflux for 4 d. Chromatography on silica gel then gave in order: 0.13 g (10%) of the known [26] yellow crystalline $[\{Ru(GeMe_3)(\mu_2\text{-}GeMe_2)(CO)_3\}_2]$, identified by i.r. spectroscopy; 4 mg of an unidentified liquid with a strong carbonyl-stretching band at 1 955 cm^{-1}; 0.10 g (8%) of yellow liquid $[Ru(GeMe_3)(CO)_2(C_8H_9)]$ (5b), identified by

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[22] R. N. Haszeldine, C. Parkinson, and P. J. Robinson, *J.C.S. Perkin II*, 1973, 1018.

[23] M. Cooke, C. R. Russ, and F. G. A. Stone, *J.C.S. Dalton*, 1975, 256.

[24] J. Gasteiger, G. E. Gream, R. Huisgen, W. E. Konz, and U. Schnegg, *Chem. Ber.*, 1971, **104**, 2412.

[25] A. C. Cope and M. R. Kinter, *J. Amer. Chem. Soc.*, 1951, **73**, 3424.

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

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

i.r., mass, and ^{1}H n.m.r. spectra;[4] 0.12 g (11%) of pale yellow *crystals* of [Ru$_2$(GeMe$_3$)$_2$(CO)$_4$(C$_8$H$_6$)] (3b) (Found: C, 33.1; H, 3.7; Ge, 22.5; O, 9.8; Ru, 31.5%; *M* 652. Calc. for C$_{18}$H$_{24}$Ge$_2$O$_4$Ru$_2$: C, 33.1; H, 3.7; Ge, 22.4; O, 9.8; Ru, 31.0%; *M* 652), m.p. 235 °C (decomp.); and finally 0.09 g (9%) of golden-yellow *crystals* of [Ru$_2$(GeMe$_3$)$_2$(CO)$_4$(C$_8$H$_8$)] (13) (Found: C, 32.5; H, 3.9; Ge, 22.2; Ru, 30.7%; *M* 654. Calc. for C$_{18}$H$_{26}$Ge$_2$O$_4$Ru$_2$: C, 33.0; H, 4.0; Ge, 22.3; Ru, 30.9%; *M* 654), m.p. 215 °C (decomp.).

(*ii*) Heating (2b) (0.50 g, 1.1 mmol) with cot (0.75 g, 7.4 mmol) in hexane (80 cm^3) at reflux for 9 weeks gave, on chromatography, low yields of the complexes described in (*i*) above, but also, as a fast-moving band, white *crystals* (0.02 g, 4%) of [Ru(GeMe$_3$)(CO)$_2${C$_8$H$_8$(GeMe$_3$)}] (4b) (Found: *M* 498. Calc. for C$_{16}$H$_{26}$Ge$_2$O$_2$Ru: *M* 498), further identified by i.r. and n.m.r. spectra (see Table 3).

(*c*) [Ru(SiMe$_3$)(GeMe$_3$)(CO)$_4$] (2c). (*i*) Complex (2c) (0.3 g, 0.7 mmol) and cot (0.65 g, 6.3 mmol) were heated in hexane (85 cm^3) at reflux for 48 h. Chromatography on Florisil then gave in turn a small amount of an inseparable mixture of unidentified compounds, and a yellow oil. On sublimation at 55 °C (10^{-1} mmHg) the latter yielded to a water-cooled probe white *crystals* of [Ru(GeMe$_3$)(CO)$_2${C$_8$H$_8$(SiMe$_3$)}] (4c) (0.18 g, 54%) (Found: C, 43.1; H, 6.0%; *M* 454. Calc. for C$_{16}$H$_{26}$GeO$_4$RuSi: C, 42.3; H, 5.7%; *M* 454).

(*ii*) The same quantities of reactants heated in heptane (85 cm^3) for 46 h yielded on chromatography (4c) (0.10 g, 30%), (5b) (0.045 g, 16%), and a trace amount of (3b), each identified by i.r. spectroscopy.

(*iii*) In octane (85 cm^3) these same reactants gave, after heating for 21 h, (5b) (0.02 g, 7%) and (3b) (0.02 g, 8%), identified by i.r. spectroscopy.

Reactions of [Ru(SiMe$_3$)$_2$(CO)$_4$] (2a) *with Substituted Cyclo-octatetraenes*.—*With* C$_8$H$_7$(SiMe$_3$). Complex (2a) (2.0 g, 5.6 mmol) and C$_8$H$_7$(SiMe$_3$) (1.0 g, 5.7 mmol) were heated in hexane (50 cm^3) at reflux for 8 d, then chromatographed with hexane, giving in order: white *crystals* of [Ru(SiMe$_3$)(CO)$_2${C$_8$H$_7$(SiMe$_3$)$_2$}] (9a) (1.4 g, 52%) (Found: C, 48.1; H, 7.3%; *M* 480. Calc. for C$_{19}$H$_{34}$O$_2$RuSi$_3$: C, 47.6; H, 7.1%; *M* 480); a colourless *oil* (0.15 g, 6%) identified as a ring-substituted trimethylsilyl derivative of (5a) of formulation [Ru(SiMe$_3$)(CO)$_2${C$_8$H$_8$(SiMe$_3$)}] (Found: *M* 408. Calc. for C$_{16}$H$_{26}$O$_2$RuSi$_2$: *M* 408), ν(CO) in hexane at 2 004s and 1 949s cm^{-1}; yellow crystalline [Ru$_3$(CO)$_8${C$_8$H$_3$(SiMe$_3$)$_3$}] (0.049 g, 3%); and yellow crystalline [Ru$_3$(CO)$_8${C$_8$H$_4$(SiMe$_3$)$_2$}] (0.149 g, 10%). The two triruthenium pentalene complexes[28] eluted late from the column and were identified by comparison of their i.r. and n.m.r. spectra with those of authentic samples.

With C$_8$H$_7$Me. Complex (2a) (0.5 g, 1.4 mmol) and C$_8$H$_7$Me (1.0 g, 8.5 mmol) were heated in hexane (25 cm^3) for 4 d. Chromatography then gave in turn white *crystals* of [Ru(SiMe$_3$)(CO)$_2${C$_8$H$_7$Me(SiMe$_3$)}] (9b) (0.5 g, 85%) (Found: C, 48.7; H, 6.6%; *M* 421. Calc. for C$_{17}$H$_{29}$O$_2$RuSi$_2$: C, 48.7; H, 6.7%; *M* 421), and a colourless liquid (0.01 g, 3%) identified as a ring-substituted methyl derivative of (5a) of formulation [Ru(SiMe$_3$)(CO)$_2$(C$_8$H$_8$Me)] (Found: *M* 349. Calc. for C$_{14}$H$_{20}$O$_2$RuSi: *M* 349), ν(CO) in hexane at 2 007s and 1 950s cm^{-1}.

With C$_8$H$_7$Ph. (*i*) Complex (2a) (0.5 g, 1.4 mmol) and C$_8$H$_7$Ph (1.5 g, 8.3 mmol) were heated in hexane (50 cm^3) at reflux for 55 h. The two products of the reaction, phenyl-substituted (4a) and (5a) respectively, were not cleanly separated, but after repeated chromatography mixtures strongly enriched in each of [Ru(SiMe$_3$)(CO)$_2${C$_8$H$_7$Ph(SiMe$_3$)}] (9c) (Found: *M* 483. Calc. for C$_{22}$H$_{31}$O$_2$RuSi$_2$: *M* 483), ν(CO) in hexane at 2 014s and 1 961s cm^{-1}, and [Ru(SiMe$_3$)(CO)$_2$(C$_8$H$_8$Ph)] (Found: *M* 411. Calc. for C$_{19}$H$_{22}$O$_2$RuSi: *M* 411), ν(CO) in hexane at 2 009s and 1 953s cm^{-1}, were obtained.

(*ii*) Complex (2a) (0.5 g, 1.4 mmol) and C$_8$H$_7$Ph (1.5 g, 8.3 mmol) heated in octane (50 cm^3) for 17 h, and subsequently chromatographed, gave a trace amount of [Ru(SiMe$_3$)(CO)$_2$(C$_8$H$_8$Ph)] as above, then white crystals of [Ru$_2$(SiMe$_3$)$_2$(CO)$_4$(C$_8$H$_5$Ph)] (14c) (0.05 g, 11%) (Found: C, 45.4; H, 4.5%; *M* 638. Calc. for C$_{24}$H$_{28}$O$_4$Ru$_2$Si$_2$: C, 45.1; H, 4.4%; *M* 638), m.p. 174 °C (decomp.).

Thermolyses of Complexes [Ru(SiMe$_3$)(CO)$_2${C$_8$H$_7$R(SiMe$_3$)}].—(*a*) [Ru(SiMe$_3$)(CO)$_2${C$_8$H$_8$(SiMe$_3$)}] (4a). (*i*) Complex (4a) (1.5 g, 3.7 mmol) was heated in octane (50 cm^3) at reflux for 2 h. Infrared spectra recorded during the course of the reaction revealed a broad band at 2 120 cm^{-1}, typical of ν(SiH), which disappeared when the i.r. sample was placed under low vacuum and then rescanned, indicating evolution of SiHMe$_3$. Chromatography of the reaction mixture yielded a trace amount of (5a) and 0.39 g (37%) of [Ru$_2$(SiMe$_3$)$_2$(CO)$_4$(C$_8$H$_6$)] (3a), identified by its i.r. and n.m.r. spectra.

(*ii*) After heating (4a) (1.5 g, 3.7 mmol) in octane (50 cm^3) for 2 h exactly as in (*i*) above, excess of [Fe$_2$(CO)$_9$] was added and the mixture heated for a further 2 h. Chromatography then gave the two products as in (*i*), but with an additional yellow waxy solid mixed with (5a). Repeated sublimation (50 °C, 10^{-1} mmHg) eventually yielded this new product in low yield and contaminated with $<20\%$ of (5a). It was identified as [Fe(CO)$_3${C$_8$H$_9$(SiMe$_3$)}] on the basis of mass (Found: *M* 318. Calc. for C$_{14}$H$_{18}$FeO$_3$Si: *M* 318), i.r. [ν(CO) in hexane at 2 025s, 1 965s, and 1 953s cm^{-1}], and ^{1}H n.m.r. [τ 6.0 (2 H, m), 7.1—8.2(7 H, m), and 10.0(9 H, s) in CDCl$_3$] spectra.

In a separate control experiment (4a) was found not to react with [Fe$_2$(CO)$_9$] under the above conditions.

(*b*) [Ru(SiMe$_3$)(CO)$_2${C$_8$H$_7$(SiMe$_3$)$_2$}] (9a). Complex (9a) (0.88 g, 1.8 mmol) was heated in octane (50 cm^3) at reflux for 5 h, yielding a red air-sensitive solution. Chromatography under nitrogen then gave in turn a small amount of trimethylsilyl-substituted (5a), identified by i.r. and mass spectra, and white *crystals* (115 mg, 20%) of [Ru$_2$(SiMe$_3$)$_2$(CO)$_4${C$_8$H$_5$(SiMe$_3$)}] (14a), slightly air-sensitive as a solid (Found: C, 39.8; H, 4.9%; *M* 635. Calc. for C$_{21}$H$_{32}$O$_4$Ru$_2$Si$_3$: C, 39.7; H, 5.0%; *M* 635), m.p. 140 °C (decomp.).

(*c*) [Ru(SiMe$_3$)(CO)$_2${C$_8$H$_7$Me(SiMe$_3$)}] (9b). The complex (0.4 g, 1.0 mmol) was heated in octane (25 cm^3) at reflux for 4.5 h, then chromatographed to give a trace amount of methyl-substituted (5a), identified by i.r. and mass spectra, and 65 mg (25%) of white *crystals* of [Ru$_2$(SiMe$_3$)$_2$(CO)$_4$(C$_8$H$_5$Me)] (14b) (Found: C, 40.6; H, 4.9%; *M* 577. Calc. for C$_{19}$H$_{26}$O$_4$Ru$_2$Si$_2$: C, 39.6; H, 4.5%; *M* 577).

X-*Ray Data Collection and Structure Determination*.—Crystals of [Ru(SiMe$_3$)(CO)$_2$(C$_8$H$_8$SiMe$_3$)] (4a) grow as almost colourless rectangular plates. Diffracted intensities were collected from a crystal of dimensions 0.35 × 0.125 × 0.45 mm on a Syntex $P2_1$ four-circle diffractometer according to methods described earlier.[29] Of the total 3 442

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[28] S. A. R. Knox, R. J. McKinney, V. Riera, F. G. A. Stone, and A. C. Szary, *J.C.S. Dalton*, unpublished work.

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

reflections (complete for $2.9 \leqslant 2\theta \leqslant 50.0°$), 3 146 satisfied the criterion $I \geqslant 2.5\ \sigma(I)$ and only these were used in the solution and refinement of the structure.

Crystal data. $C_{16}H_{25}O_2RuSi_2$, $M = 406.6$, Triclinic, $a = 9.972(3)$, $b = 16.082(6)$, $c = 6.662(2)$ Å, $\alpha = 89.46(2)$, $\beta = 110.44(2)$, $\gamma = 82.46(2)°$, $U = 990.7$ Å^3, $D_m = 1.34$, $Z = 2$, $D_c = 1.36$ g cm^{-3}, $F(000) = 418$. Space group $P\bar{1}$, Mo-K_α X-radiation (graphite monochromator), $\lambda = 0.710\ 69$ Å, μ(Mo-K_α) $= 9.19$ cm^{-1}.

The structure was solved by conventional heavy-atom methods, and in the final refinement (by blocked-matrix least squares) anisotropic thermal parameters were used for all the non-hydrogen atoms. Hydrogen atoms were incorporated at positions estimated from the electron-density maps and were refined with isotropic thermal parameters. Weights were applied according to the scheme $1/w = \sigma(F)^2$. The refinement converged to R 0.035 (R' 0.045), and a final electron-density difference synthesis showed no peaks >0.7 or < -0.5 eÅ^{-3}. The data were corrected for X-ray absorption,[30] and the atomic-scattering factors were those of ref. 31 for hydrogen and ref. 32 for all the other atoms. In the case of Ru and Si these were corrected for the real and imaginary parts of anomalous dispersion.[33] Positional parameters are in Table **1**, bond lengths and angles in Table 2. All the computational work was carried out at the University of London Computing Centre with the 'X-Ray' system of programs.[30] Observed and calculated structure factors and thermal parameters are listed in Supplementary Publication No. SUP 22204 (20 pp.).*

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* For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1977, Index issue.

[30] Technical Report TR192, Computer Science Centre, University of Maryland, June 1972.

[31] R. F. Stewart, E. R. Davidson, and W. Simpson, *J. Chem. Phys.*, 1965, **42**, 3175.

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

[33] 'International Tables for X-Ray Crystallography,' Kynoch Press, Birmingham, 1974, vol. 4.