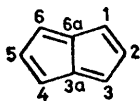


## Pentalene Complexes of Ruthenium: Two Isomeric forms of Triruthenium Carbonyl Clusters with Face- and Edge-bridging Pentalene Ligands: Crystal Structures of Two Isomers of $[\text{Ru}_3(\text{CO})_8\{\text{C}_8\text{H}_3(\text{SiMe}_3)_3-1,3,5\}]$

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The complexes  $[\text{Ru}_3(\text{CO})_8\{\text{C}_8\text{H}_3(\text{SiMe}_3)_3-1,3,5\}]$  exist in two isomeric forms which have been characterised by X-ray diffraction. In one of the isomers (A) only two ruthenium atoms of the  $\text{Ru}_3$  triangle are directly bonded to the pentalene ligand; the geometry of the  $\text{Ru}_2$ -pentalene moiety is closely comparable with that established for  $[\text{Ru}_2(\text{GeMe}_3)_2(\text{CO})_4(\text{C}_8\text{H}_6)]$ . This edge-bridging isomer is fluxional but with a free energy of activation substantially less than that of the unsubstituted species  $[\text{Ru}_3(\text{CO})_8(\text{C}_8\text{H}_6)]$ . The two Ru atoms which are bonded to the pentalene each carry two CO groups, while the Ru atom not so bonded carries four. Crystals of (A) are yellow, monoclinic, space group  $P2_1/c$ , with  $Z = 4$  in a unit cell of dimensions  $a = 16.264(8)$ ,  $b = 9.023(3)$ ,  $c = 22.770(9)$  Å, and  $\beta = 97.95(4)^\circ$ ; despite the different activation energy, the angle between the  $\text{Ru}_3$  plane and that of the pentalene is much the same as in  $[\text{Ru}_3(\text{CO})_8(\text{C}_8\text{H}_6)]$  (*ca.*  $50^\circ$ ). In the other isomer (B) all three atoms of the  $\text{Ru}_3$  triangle are directly bonded to the pentalene ligand in a symmetrical parallel orientation; this necessitates rearrangement of the CO ligands. The Ru atom which is centrally placed with respect to the pentalene ligand now carries only two CO groups, while the flanking Ru atoms carry three each. Crystals of (B) are orange-red, monoclinic, space group  $P2_1/n$ , with  $Z = 4$  in a unit cell of dimensions  $a = 11.488(3)$ ,  $b = 18.646(7)$ ,  $c = 15.379(7)$  Å, and  $\beta = 90.99(3)^\circ$ . Both structures have been solved by heavy-atom methods from data collected on a Syntex  $P2_1$  four-circle diffractometer. For (A) the 7 701 unique reflections refined to  $R$  0.039 ( $R'$  0.047), and for (B) the 3 588 unique reflections gave  $R$  0.037 ( $R'$  0.044).

THE first complex of pentalene was prepared in 1972 by reaction of cyclo-octatetraene with *cis*- $[\text{Ru}(\text{GeMe}_3)_2(\text{CO})_4]$ ;<sup>1</sup> the  $\text{C}_8$  ring had clearly formed a transannular bridge, giving rise to the (nearly planar) pair of fused  $\text{C}_5$  rings which characterise the pentalene ligand (see diagram with systematic numbering). An X-ray dif-



fraction study on the complex  $[\text{Ru}_2(\text{GeMe}_3)_2(\text{CO})_4(\text{C}_8\text{H}_6)]$  confirmed that the pentalene system had indeed been synthesised, and also established its detailed geometry.<sup>2,3</sup> Further synthetic work on the reaction of cyclo-octatetraene and its monosubstituted derivatives with  $[\text{Ru}_3(\text{CO})_{12}]$  in refluxing heptane or octane gave rise to another series of pentalene complexes  $[\text{Ru}_3(\text{CO})_8(\text{C}_8\text{H}_5\text{R})]$  ( $\text{R} = \text{H}, \text{Me}, \text{or Ph}$ ). A crystal-structure determination on  $[\text{Ru}_3(\text{CO})_8(\text{C}_8\text{H}_6)]$  revealed<sup>4</sup> that only *two* ruthenium atoms of the  $\text{Ru}_3$  triangle were bonded to the pentalene moiety, but the manner of bonding was closely similar to that already established for  $[\text{Ru}_2(\text{GeMe}_3)_2(\text{CO})_4(\text{C}_8\text{H}_6)]$ . Remarkably, however, the  $\text{Ru}_3$  triangle is at an angle of *ca.*  $50^\circ$  to the mean plane of the pentalene system. The potential fluxional properties of such molecules have already been discussed in detail.<sup>5,6</sup>

We now report a surprising development in pentalene chemistry. Reaction of ring-substituted cyclo-octatrienes with  $[\text{Ru}_3(\text{CO})_{12}]$  gives rise to pentalene complexes, and their formation is favoured when the ring substituent is the trimethylsilyl group.<sup>7,8</sup> In particular, reaction of 2,5,8-tris(trimethylsilyl)cyclo-octa-1,3,6-triene with  $[\text{Ru}_3(\text{CO})_{12}]$  in refluxing heptane yields (*ca.* 10%)  $[\text{Ru}_3(\text{CO})_8\{\text{C}_8\text{H}_3(\text{SiMe}_3)_3-1,3,5\}]$ . Remarkably, the first crystal (B) of this complex to be examined had a structure quite different from that reported for  $[\text{Ru}_3(\text{CO})_8(\text{C}_8\text{H}_6)]$ .

Further examination showed, however, that  $[\text{Ru}_3(\text{CO})_8\{\text{C}_8\text{H}_3(\text{SiMe}_3)_3-1,3,5\}]$  exists in two isomeric forms, the second of which (A) has a structure similar to that already reported for  $[\text{Ru}_3(\text{CO})_8(\text{C}_8\text{H}_6)]$ . The structures of these two isomers form the subject of the diffraction studies described in this paper; a preliminary report of the work has been given.<sup>9</sup>

### EXPERIMENTAL

Crystals of  $[\text{Ru}_3(\text{CO})_8\{\text{C}_8\text{H}_3(\text{SiMe}_3)_3-1,3,5\}]$  were obtained from hexane solution; it transpired in the course of the investigation that the crystals are of two types, and although both might be described as orange-yellow closer examination showed that those of isomer (B) are somewhat darker in colour. The greater part of the sample was composed of (A), and a structure determination on a crystal of (A) gave the result that had been expected from the spectral examination. In the light of the results from (B), however, it proved possible to reappraise and reinterpret the i.r. spectrum of the hexane solution, in which both isomers exist in equilibrium.

A crystal of (A) was sealed into a Lindemann capillary and cooled to 160 K on a Syntex  $P2_1$  four-circle diffractometer. Intensities were collected to  $2\theta = 60^\circ$ , with three check reflections remeasured after every 40 intensities. Monochromatised Mo- $K_\alpha$  X-radiation was used. Of the 10 632 reflections measured, 7 701 were independent and satisfied the criterion  $I \geq 2.0\sigma(I)$ , and only these were used in the solution and refinement of the structure. There was no evidence for crystal decay, and no correction for X-ray absorption was made.

For crystal (B) similar conditions were used, except that measurements were made at room temperature 298 K,  $2\theta_{\text{max}}$  was  $50^\circ$ , check reflections were remeasured every 30 intensities, and of the 5 138 reflections measured, 3 588 were independent and had  $I > 2.5\sigma(I)$ .

### RESULTS

*Crystal Data.*—(A),  $\text{C}_{25}\text{H}_{30}\text{O}_8\text{Ru}_3\text{Si}_3$ ,  $M = 846.1$ , Monoclinic,  $a = 16.264(8)$ ,  $b = 9.023(3)$ ,  $c = 22.770(9)$  Å,

$\beta = 97.95(4)^\circ$ ,  $Z = 4$ ,  $D_c = 1.70 \text{ g cm}^{-3}$ ,  $U = 3\ 309(3) \text{ \AA}^3$ ,  
 $F(000) = 1\ 672$ . Space group  $P2_1/c$  (no. 14), Mo- $K_\alpha$  X-

TABLE 1

Atomic positional co-ordinates (fractional cell co-ordinates  $\times 10^4$  except for Ru and Si,  $\times 10^5$ ) for (A), the edge-bonded isomer of  $[\text{Ru}_3(\text{CO})_8\{\text{C}_8\text{H}_3(\text{SiMe}_3)_3-1,3,5\}]$ , with estimated standard deviations in parentheses

Atom	<i>x</i>	<i>y</i>	<i>z</i>
C(1)	2 687(2)	2 285(4)	-42(2)
C(2)	3 537(2)	2 461(4)	220(2)
C(3)	3 632(2)	2 511(4)	864(2)
C(4)	2 792(2)	2 524(4)	1 006(2)
C(5)	2 308(2)	2 705(4)	1 480(2)
C(6)	1 437(2)	2 849(4)	1 226(2)
C(7)	1 378(2)	2 504(4)	609(2)
C(8)	2 213(2)	2 347(4)	456(2)
C(9)	2 589(3)	-3 052(5)	898(2)
C(10)	2 674(3)	-2 630(6)	2 104(2)
C(11)	3 351(2)	108(5)	1 998(2)
C(12)	4 180(3)	-2 220(5)	1 539(2)
C(13)	2 636(3)	-1 137(5)	-76(2)
C(14)	4 145(3)	-718(5)	381(2)
C(15)	1 149(3)	-916(5)	646(2)
C(16)	1 281(3)	-197(6)	1 778(2)
C(17)	1 228(3)	1 384(6)	-935(2)
C(18)	3 001(3)	1 480(7)	-1 294(2)
C(19)	2 112(4)	4 354(6)	-1 055(3)
C(20)	5 168(3)	4 364(6)	849(2)
C(21)	5 349(3)	1 499(6)	1 541(3)
C(22)	4 386(3)	4 082(5)	1 999(2)
C(23)	933(3)	3 381(7)	2 439(2)
C(24)	-396(3)	2 485(6)	1 402(2)
C(25)	425(3)	5 545(6)	1 432(3)
H(2)	3 990	2 533	-7
H(5)	2 516	2 709	1 893
H(7)	876	2 394	339
H(171)	1 296	383	-809
H(172)	859	1 869	-706
H(173)	1 002	1 419	-1 344
H(181)	3 517	1 982	-1 229
H(182)	3 091	461	-1 171
H(183)	2 782	1 498	-1 700
H(191)	1 738	4 830	-824
H(192)	2 630	4 870	-991
H(193)	1 889	4 409	-1 463
H(201)	5 277	3 895	498
H(202)	4 830	5 229	744
H(203)	5 675	4 677	1 079
H(211)	5 075	807	1 763
H(212)	5 475	1 022	1 188
H(213)	5 856	1 781	1 770
H(221)	4 056	4 939	1 890
H(222)	4 084	3 447	2 230
H(223)	4 889	4 378	2 236
H(231)	1 052	2 365	2 543
H(232)	1 422	3 951	2 549
H(233)	501	3 725	2 646
H(241)	-564	2 582	990
H(242)	-305	1 459	1 498
H(243)	-837	2 828	1 607
H(251)	920	6 092	1 556
H(252)	274	5 662	1 017
H(253)	-10	5 906	1 635
O(9)	2 339(3)	-4 008(5)	597(2)
O(10)	2 473(3)	-3 296(5)	2 485(2)
O(11)	3 558(2)	947(4)	2 368(2)
O(12)	4 861(2)	-2 560(4)	1 608(2)
O(13)	2 346(2)	-1 909(4)	-447(2)
O(14)	4 736(2)	-1 363(4)	312(2)
O(15)	739(2)	-1 694(5)	330(2)
O(16)	984(3)	-629(5)	2 179(2)
Ru(1)	31 645(2)	2 526(3)	4 641(1)
Ru(2)	30 475(2)	-15 399(4)	14 678(2)
Ru(3)	17 558(2)	4 899(3)	11 357(1)
Si(1)	22 481(7)	23 566(13)	-8 501(5)
Si(2)	46 362(6)	30 836(13)	13 241(5)
Si(3)	5 768(6)	35 490(14)	16 292(5)

TABLE 2

Bond distances ( $\text{\AA}$ ) and angles ( $^\circ$ ) for (A), edge-bonded  $[\text{Ru}_3(\text{CO})_8\{\text{C}_8\text{H}_3(\text{SiMe}_3)_3-1,3,5\}]$ , with estimated standard deviations in parentheses

(i) Distances			
(a) Metal-metal			
Ru(1)-Ru(2)	2.838(6)	Ru(3)-Ru(1)	2.933(48)
Ru(2)-Ru(3)	2.811(23)		
(b) Carbonyls			
Ru(2)-C(9)	1.957(20)	C(9)-O(9)	1.142(12)
Ru(2)-C(10)	1.918(19)	C(10)-O(10)	1.140(12)
Ru(2)-C(11)	1.936(13)	C(11)-O(11)	1.148(11)
Ru(2)-C(12)	1.927(8)	C(12)-O(12)	1.139(8)
Ru(1)-C(13)	1.879(23)	C(13)-O(13)	1.145(15)
Ru(1)-C(14)	1.852(8)	C(14)-O(14)	1.153(8)
Ru(3)-C(15)	1.877(24)	C(15)-O(15)	1.150(18)
Ru(3)-C(16)	1.852(25)	C(16)-O(16)	1.158(17)
(c) Pentalene			
C(1)-C(2)	1.436(24)	C(5)-C(6)	1.460(23)
C(2)-C(3)	1.454(8)	C(6)-C(7)	1.430(7)
C(3)-C(4)	1.447(13)	C(7)-C(8)	1.454(14)
C(4)-C(5)	1.430(24)	C(8)-C(1)	1.457(25)
C(4)-C(8)	1.469(33)		
(d) Si-C			
Si(1)-C(1)	1.882(28)	Si(2)-C(20)	1.875(21)
Si(2)-C(3)	1.886(36)	Si(2)-C(21)	1.863(13)
Si(3)-C(6)	1.886(28)	Si(2)-C(22)	1.875(14)
Si(1)-C(17)	1.863(9)	Si(3)-C(23)	1.861(24)
Si(1)-C(18)	1.867(27)	Si(3)-C(24)	1.862(18)
Si(1)-C(19)	1.867(6)	Si(3)-C(25)	1.864(6)
(e) Ru-pentalene			
Ru(1)-C(1)	2.246(16)	Ru(3)-C(4)	2.536(9)
Ru(1)-C(2)	2.177(7)	Ru(3)-C(5)	2.285(13)
Ru(1)-C(3)	2.317(13)	Ru(3)-C(6)	2.207(4)
Ru(1)-C(4)	2.510(13)	Ru(3)-C(7)	2.217(14)
Ru(1)-C(8)	2.441(4)	Ru(3)-C(8)	2.464(19)
(ii) Angles			
(a) Ru triangle			
Ru(3)-Ru(1)-Ru(2)	58.4(0)	Ru(2)-Ru(3)-Ru(1)	58.9(0)
Ru(1)-Ru(2)-Ru(3)	62.7(0)		
(b) Carbonyls			
Ru(2)-C(9)-O(9)	175.1(4)	Ru(1)-C(13)-O(13)	173.4(4)
Ru(2)-C(10)-O(10)	178.1(4)	Ru(1)-C(14)-O(14)	177.1(4)
Ru(2)-C(11)-O(11)	171.1(4)	Ru(3)-C(15)-O(15)	174.9(4)
Ru(2)-C(12)-O(12)	175.9(4)	Ru(3)-C(16)-O(16)	179.9(4)
C(9)-Ru(2)-Ru(3)	94.2(1)	C(10)-Ru(2)-C(12)	99.9(2)
C(9)-Ru(2)-C(10)	90.7(2)	C(10)-Ru(2)-Ru(1)	165.4(1)
C(9)-Ru(2)-C(11)	171.7(2)	C(11)-Ru(2)-Ru(3)	77.5(1)
C(9)-Ru(2)-C(12)	96.1(2)	C(11)-Ru(2)-C(12)	91.9(2)
C(9)-Ru(2)-Ru(1)	85.7(2)	C(11)-Ru(2)-Ru(1)	91.4(1)
C(10)-Ru(2)-Ru(3)	103.6(1)	C(12)-Ru(2)-Ru(3)	154.2(1)
C(10)-Ru(2)-C(11)	90.2(2)	C(12)-Ru(2)-Ru(1)	94.6(1)
Ru(3)-Ru(1)-C(13)	94.1(2)	C(14)-Ru(1)-Ru(2)	97.6(2)
C(13)-Ru(1)-C(14)	86.5(2)		
Ru(1)-Ru(3)-C(15)	91.4(1)	C(16)-Ru(3)-Ru(2)	87.0(1)
C(15)-Ru(3)-C(16)	90.1(2)		
(c) Pentalene			
C(8)-C(1)-C(2)	104.8(3)	C(4)-C(5)-C(6)	108.4(3)
C(1)-C(2)-C(3)	112.6(3)	C(5)-C(6)-C(7)	107.4(3)
C(2)-C(3)-C(4)	104.7(3)	C(6)-C(7)-C(8)	108.6(3)
C(3)-C(4)-C(8)	108.8(3)	C(7)-C(8)-C(4)	107.2(3)
C(8)-C(4)-C(5)	107.5(3)	C(4)-C(8)-C(1)	108.7(3)
(d) About Si			
C(1)-Si(1)-C(17)	107.3(2)	C(17)-Si(1)-C(18)	112.7(2)
C(1)-Si(1)-C(18)	109.1(2)	C(18)-Si(1)-C(19)	109.7(3)
C(1)-Si(1)-C(19)	107.1(2)	C(19)-Si(1)-C(17)	110.8(2)
C(3)-Si(2)-C(20)	106.4(2)	C(20)-Si(2)-C(21)	107.8(2)
C(3)-Si(2)-C(21)	113.3(2)	C(21)-Si(2)-C(22)	110.5(2)
C(3)-Si(2)-C(22)	108.5(2)	C(22)-Si(2)-C(20)	110.3(2)
C(6)-Si(3)-C(23)	107.7(2)	C(23)-Si(3)-C(24)	111.7(3)
C(6)-Si(3)-C(24)	110.6(2)	C(24)-Si(3)-C(25)	111.6(2)
C(6)-Si(3)-C(25)	106.8(2)	C(25)-Si(3)-C(23)	109.3(3)

TABLE 3

Equations of some least-squares planes for edge-bonded isomer (A): distances (Å) of relevant atoms from these planes are given in square brackets ( $x, y, z$  are fractional crystal co-ordinates)

Plane (1): Ru(1), Ru(2), Ru(3)

$$6.758x + 6.258y + 11.963z = 2.852$$

[C(10) -0.174, C(12) 0.426, C(14) -0.045, C(16) 0.018]

Plane (2): C(1), C(2), C(3), C(4), C(8)

$$-0.792x + 8.985y - 1.586z = 1.865$$

[C(1) -0.175, C(2) 0.032, C(3) -0.033, C(4) 0.022, C(8) -0.004, Si(1) 0.210, Si(2) 0.329, Ru(1) -1.962]

Plane (3): C(4), C(5), C(6), C(7), C(8)

$$1.379x + 8.882y - 3.740z - 2.219$$

[C(4) 0.032, C(5) -0.052, C(6) 0.052, C(7) -0.032, C(8) 0.000, Si(3) 0.404, Ru(3) -1.966]

Plane (4): C(1)-C(8)

$$0.310x + 8.964y - 2.587z - 2.151$$

[C(1) -0.008, C(2) 0.108, C(3) -0.011, C(4) -0.062, C(5) -0.038, C(6) 0.130, C(7) -0.021, C(8) -0.097]

Angles (°) between least-squares planes:

(1)-(2)	51.3	(1)-(4)	50.9
(1)-(3)	51.1	(2)-(3)	8.9

radiation (graphite monochromator),  $\lambda = 0.71069$  Å,  $\mu(\text{Mo-K}\alpha) = 14.8$  cm<sup>-1</sup>.

(B).  $a = 11.488(3)$ ,  $b = 18.646(7)$ ,  $c = 15.379(7)$  Å,  $\beta = 90.99(3)^\circ$ ,  $D_c = 1.71$  g cm<sup>-3</sup>,  $U = 3294(2)$  Å<sup>3</sup>, space group  $P2_1/n$ ; all other details as for (A).

For both crystals the three ruthenium atoms were located by vector methods and the remaining non-hydrogen atoms by successive electron-density difference syntheses. The structures were refined by blocked-matrix least squares, using anisotropic thermal parameters for all atoms except the eight C atoms of the pentalene moiety. Hydrogen atoms were incorporated into the structure at calculated positions but were not refined ( $U_{\text{iso}} = 0.076$ ). Atomic scattering factors were those of ref. 10 for C, O, Ru, and Si, and of ref. 11 for H. No corrections were made for anomalous dispersion. Weights were applied according to the scheme:  $w^{-1} = a + b(F) + c(F)^2 + d(F)^3$  with, for (A),  $a = 3.9$ ,  $b = 8.3 \times 10^{-2}$ ,  $c = 8.0 \times 10^{-4}$ , and  $d = 1.0 \times 10^{-6}$ ; for (B),  $a = 4.4$ ,  $b = -6.7 \times 10^{-2}$ ,  $c = 4.0 \times 10^{-4}$ , and  $d = 0$ . These gave satisfactory weight analyses. Refinement converged at  $R$  0.039 ( $R' = 0.047$ ) for (A) and at 0.037 (0.044) for (B). The mean shift-to-error ratios in the final cycles were 0.007 (A) and 0.068 (B), and the final electron-density difference maps showed no peaks  $>1.0$  or  $< -0.5$  e Å<sup>-3</sup> for (A) and none  $>0.5$  or  $< -0.5$  e Å<sup>-3</sup> for (B). Positional parameters are in Tables 1 and 4, interatomic distances and bond angles in Tables 2 and 5, and some least-squares planes and dihedral angles in Tables 3 and 6 for (A) and (B) respectively. All the computational work was carried out at the University of London Computer Centre with the 'X-Ray' system of programs.<sup>12</sup> Observed and calculated structure factors, and all thermal parameters, are listed in Supplementary Publication No. SUP 22581 (48 pp.).\*

#### DISCUSSION

The molecular structure of the edge-bonded isomer (A) is shown in Figures 1 and 2, which also include the

\* For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1978, Index issue.

crystallographic numbering system. In Figure 1 the molecule is seen perpendicular to the mean plane of the

TABLE 4

Atomic positional co-ordinates (fractional cell co-ordinates  $\times 10^4$  except for Ru,  $\times 10^5$ ) for (B), the face-bonded isomer of  $[\text{Ru}_3(\text{CO})_8(\text{C}_8\text{H}_3(\text{SiMe}_3)_3-1,3,5)]$ , with estimated standard deviations in parentheses

Atom	$x$	$y$	$z$
C(1)	2 391(6)	3 015(4)	250(4)
C(2)	1 479(6)	2 761(4)	823(4)
C(3)	961(6)	2 087(4)	596(4)
C(4)	1 650(6)	1 855(3)	-146(4)
C(5)	1 870(6)	1 255(4)	-693(4)
C(6)	2 813(6)	1 414(4)	-1 262(4)
C(7)	3 197(6)	2 121(4)	-1 033(4)
C(8)	2 493(5)	2 396(3)	-358(4)
C(9)	5 077(6)	1 520(4)	229(5)
C(10)	3 590(7)	486(4)	585(5)
C(11)	4 905(7)	3 166(5)	661(5)
C(12)	3 372(8)	3 311(5)	2 119(6)
C(13)	4 830(8)	2 178(5)	1 999(6)
C(14)	1 097(7)	734(5)	1 656(5)
C(15)	1 385(7)	1 985(5)	2 624(5)
C(16)	3 236(7)	1 098(5)	2 339(5)
C(17)	3 475(10)	4 024(5)	-1 060(7)
C(18)	2 834(10)	4 632(5)	711(7)
C(19)	956(9)	4 205(5)	-566(7)
C(20)	-1 332(7)	1 982(5)	1 637(6)
C(21)	-984(7)	1 055(5)	36(6)
C(22)	-1 278(8)	2 656(6)	-164(7)
C(23)	2 326(9)	983(5)	-3 098(6)
C(24)	3 222(8)	-140(5)	-1 795(6)
C(25)	4 837(7)	1 044(5)	-2 427(6)
H(2)	1 201	3 043	1 312
H(5)	1 430	799	-672
H(7)	3 835	2 388	-1 301
H(171)	4 240	3 889	-873
H(172)	3 234	3 725	-1 529
H(173)	3 506	4 513	-1 268
H(181)	2 254	4 623	1 162
H(182)	3 563	4 538	954
H(183)	2 838	5 137	519
H(191)	733	3 898	-1 032
H(192)	398	4 164	-1 195
H(193)	967	4 691	-765
H(201)	-1 000	1 628	2 015
H(202)	-1 197	2 446	1 894
H(203)	-2 164	1 909	1 630
H(211)	-709	1 031	-542
H(212)	-645	671	366
H(213)	-1 821	964	8
H(221)	-1 109	3 121	68
H(222)	-967	2 630	-738
H(223)	-2 099	2 586	-195
H(231)	1 520	857	-2 955
H(232)	2 317	1 469	-3 278
H(233)	2 557	679	-3 560
H(241)	3 695	-229	-1 290
H(242)	2 438	-268	-1 673
H(243)	3 489	-457	-2 251
H(251)	4 884	1 526	-2 612
H(252)	5 335	976	-1 929
H(253)	5 113	739	-2 883
O(9)	6 068(5)	1 565(4)	230(5)
O(10)	3 674(6)	-91(3)	803(4)
O(11)	5 637(6)	3 451(4)	336(5)
O(12)	3 185(8)	3 704(4)	2 661(5)
O(13)	5 569(6)	1 974(4)	2 437(5)
O(14)	556(6)	230(4)	1 751(5)
O(15)	1 021(6)	2 221(4)	3 234(4)
O(16)	3 853(6)	773(4)	2 774(5)
Ru(1)	37 076(5)	26 274(3)	12 492(4)
Ru(2)	20 813(5)	15 684(3)	16 407(4)
Ru(3)	34 607(5)	14 225(3)	1 210(3)
Si(1)	2 441(2)	3 969(1)	-142(1)
Si(2)	-667(2)	1 935(1)	546(1)
Si(3)	3 328(2)	814(1)	-2 154(1)

TABLE 5

Bond distances (Å) and angles (°) for (B), face-bonded  $[\text{Ru}_3(\text{CO})_8(\text{C}_8\text{H}_8(\text{SiMe}_3)_3-1,3,5)]$ , with estimated standard deviations in parentheses

## (i) Distances

## (a) Metal-metal

Ru(1)–Ru(2)	2.791(12)	Ru(3)–Ru(1)	2.850(5)
Ru(2)–Ru(3)	2.859(40)		

## (b) Carbonyls

Ru(3)–C(9)	1.870(9)	C(9)–O(9)	1.142(9)
Ru(3)–C(10)	1.891(8)	C(10)–O(10)	1.131(10)
Ru(1)–C(11)	1.939(21)	C(11)–O(11)	1.120(16)
Ru(1)–C(12)	1.893(12)	C(12)–O(12)	1.133(12)
Ru(1)–C(13)	1.909(25)	C(13)–O(13)	1.140(19)
Ru(2)–C(14)	1.923(9)	C(14)–O(14)	1.138(11)
Ru(2)–C(15)	1.889(21)	C(15)–O(15)	1.125(15)
Ru(2)–C(16)	1.906(24)	C(16)–O(16)	1.141(17)

## (c) Pentalene

C(1)–C(2)	1.459(22)	C(5)–C(6)	1.435(22)
C(2)–C(3)	1.431(11)	C(6)–C(7)	1.432(10)
C(3)–C(4)	1.465(21)	C(7)–C(8)	1.423(20)
C(4)–C(5)	1.425(10)	C(8)–C(1)	1.490(10)
C(4)–C(8)	1.440(11)		

## (d) Si–C

Si(1)–C(1)	1.881(7)	Si(2)–C(20)	1.857(23)
Si(2)–C(3)	1.892(7)	Si(2)–C(21)	1.853(11)
Si(3)–C(6)	1.874(15)	Si(2)–C(22)	1.862(17)
Si(1)–C(17)	1.863(30)	Si(3)–C(23)	1.864(29)
Si(1)–C(18)	1.852(14)	Si(3)–C(24)	1.867(9)
Si(1)–C(19)	1.868(21)	Si(3)–C(25)	1.842(15)

## (e) Ru–pentalene

Ru(1)–C(2)	1.644(21)	Ru(3)–C(4)	2.261(13)
Ru(1)–C(1)	2.257(32)	Ru(3)–C(5)	2.219(32)
Ru(1)–C(8)	2.850(38)	Ru(3)–C(6)	2.241(23)
		Ru(3)–C(7)	2.217(10)
Ru(2)–C(2)	2.642(12)	Ru(3)–C(8)	2.246(13)
Ru(2)–C(3)	2.259(29)		
Ru(2)–C(4)	2.835(16)		

## (ii) Angles

## (a) Ru triangle

Ru(3)–Ru(1)–Ru(2)	60.9(0)	Ru(2)–Ru(3)–Ru(1)	58.5(0)
Ru(1)–Ru(2)–Ru(3)	60.6(0)		

## (b) Carbonyls

Ru(3)–C(9)–O(9)	174.8(7)	Ru(1)–C(13)–O(13)	172.8(8)
Ru(3)–C(10)–O(10)	175.1(7)	Ru(2)–C(14)–O(14)	172.8(8)
Ru(1)–C(11)–O(11)	176.4(8)	Ru(2)–C(15)–O(15)	176.3(7)
Ru(1)–C(12)–O(12)	177.6(8)	Ru(2)–C(16)–O(16)	173.9(8)

C(9)–Ru(3)–C(10)	89.1(3)	C(14)–Ru(2)–C(15)	93.7(4)
C(11)–Ru(1)–C(12)	97.8(4)	C(15)–Ru(2)–C(16)	92.2(3)
C(12)–Ru(1)–C(13)	90.7(4)	C(16)–Ru(2)–C(14)	91.4(4)
C(13)–Ru(1)–C(11)	91.8(4)		

## (c) Pentalene

C(8)–C(1)–C(2)	101.2(5)	C(4)–C(5)–C(6)	109.9(6)
C(1)–C(2)–C(3)	115.9(6)	C(5)–C(6)–C(7)	105.8(6)
C(2)–C(3)–C(4)	102.8(6)	C(6)–C(7)–C(8)	109.6(6)
C(3)–C(4)–C(8)	110.1(5)	C(7)–C(8)–C(4)	107.7(5)
C(8)–C(4)–C(3)	106.9(5)	C(4)–C(8)–C(1)	109.9(5)

## (d) About Si

C(1)–Si(1)–C(17)	108.6(4)	C(17)–Si(1)–C(18)	110.4(3)
C(1)–Si(1)–C(18)	114.4(4)	C(18)–Si(1)–C(19)	107.5(3)
C(1)–Si(1)–C(19)	107.5(4)	C(19)–Si(1)–C(17)	108.2(5)
C(3)–Si(2)–C(20)	112.3(3)	C(20)–Si(2)–C(21)	110.1(4)
C(3)–Si(2)–C(21)	109.7(3)	C(21)–Si(2)–C(22)	108.8(5)
C(3)–Si(2)–C(22)	106.2(4)	C(22)–Si(2)–C(20)	109.8(4)
C(6)–Si(3)–C(23)	105.7(4)	C(23)–Si(3)–C(24)	110.4(4)
C(6)–Si(3)–C(24)	109.2(4)	C(24)–Si(3)–C(25)	110.8(4)
C(6)–Si(3)–C(25)	109.8(4)	C(25)–Si(3)–C(23)	110.7(4)

pentalene, while Figure 2 is an end-on view to show the spatial relationships of the substituents. Only two of

TABLE 6

Equation of some least-squares planes for face-bonded isomer (B)

Plane (1): Ru(1), Ru(2), Ru(3)			
$-7.897x + 9.153y - 8.046z = -1.528$			
[C(11) 0.020, C(12) 0.191, C(14) 0.002, C(15) 0.140]			
Plane (2): C(1), C(2), C(3), C(4), C(8)			
$7.566x - 8.209y + 9.208z = -0.417$			
[C(1) -0.020, C(2) 0.026, C(3) -0.021, C(4) 0.008, C(8) 0.006, Si(1) -1.126, Si(2) -1.174, Ru(1) 2.215, Ru(2) 2.215]			
Plane (3): C(4), C(5), C(6), C(7), C(8)			
$7.201x - 7.041y + 10.313z = -0.261$			
[C(4) -0.007, C(5) 0.010, C(6) -0.010, C(7) 0.006, C(8) 0.001, Si(3) -0.136, Ru(3) 1.877]			
Plane (4): C(1)–C(8)			
$-7.379x + 7.598y - 9.811z = 0.274$			
[C(1) 0.007, C(2) -0.075, C(3) 0.018, C(4) 0.060, C(5) -0.021, C(6) -0.038, C(7) -0.009, C(8) 0.056]			
Angles (°) between least-squares planes:			
(1)–(2)	5.4	(1)–(4)	8.5
(1)–(3)	11.1	(2)–(3)	5.7

the three ruthenium atoms are directly bonded to the pentalene; the Ru–Ru distance for this pair is 2.93(1) Å, indistinguishable from the value of 2.94(1) found<sup>4</sup> in  $[\text{Ru}_3(\text{CO})_8(\text{C}_8\text{H}_6)]$  but notably shorter than that found in the binuclear complex  $[\text{Ru}_2(\text{GeMe}_3)_2(\text{CO})_4(\text{C}_8\text{H}_6)]$  [3.058(4) Å].<sup>3</sup> If we describe the bonding between the Ru atoms and the pentalene in the same general terms as for the binuclear species, we may regard atoms C(1)–C(3) and C(5)–C(7), simplistically, as interannular  $\pi$ -allyl units bonded only to Ru(1) and Ru(3), respectively, while the bridge carbon atoms C(4) and C(8) form a four-electron-four-atom system with the two metal

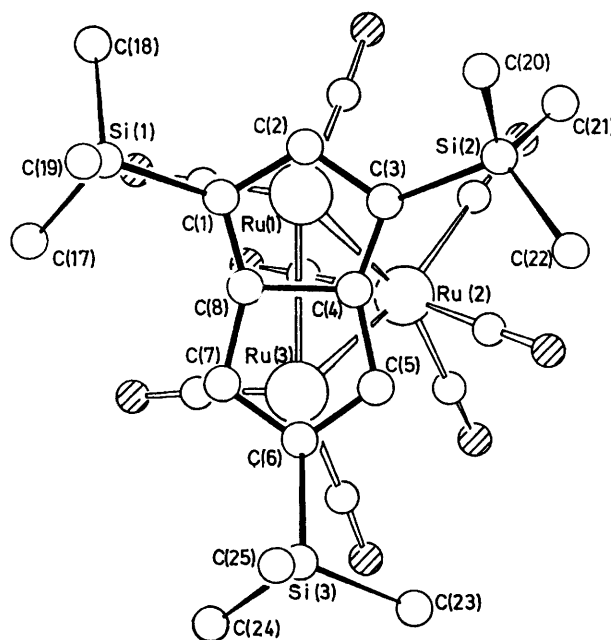


FIGURE 1 Molecular structure of the edge-bonded isomer (A) of  $[\text{Ru}_3(\text{CO})_8(\text{C}_8\text{H}_8(\text{SiMe}_3)_3-1,3,5)]$ , viewed perpendicular to the plane of the pentalene moiety, and showing the crystallographic atom-numbering sequence

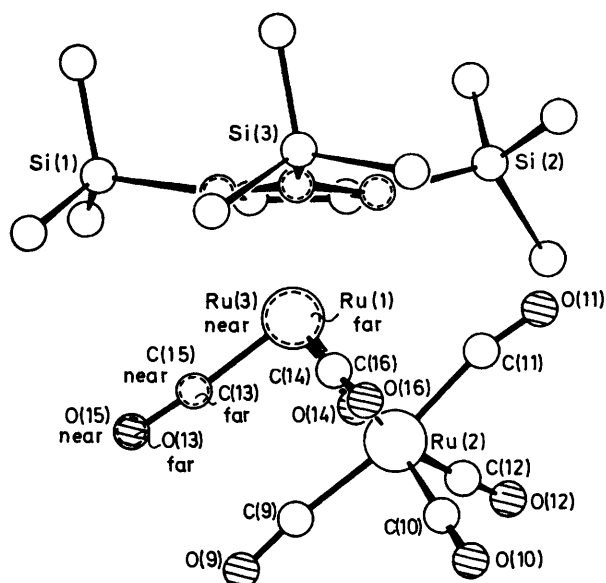


FIGURE 2 Molecular structure of the edge-bonded isomer (A) seen along the vector joining the two ruthenium atoms which are bonded to the pentalene

atoms. The mean Ru-C(allyl) distance is  $2.24_1$  Å and the mean Ru-C(bridge) distance  $2.48_8$  Å, respectively longer and shorter than in the binuclear complex where

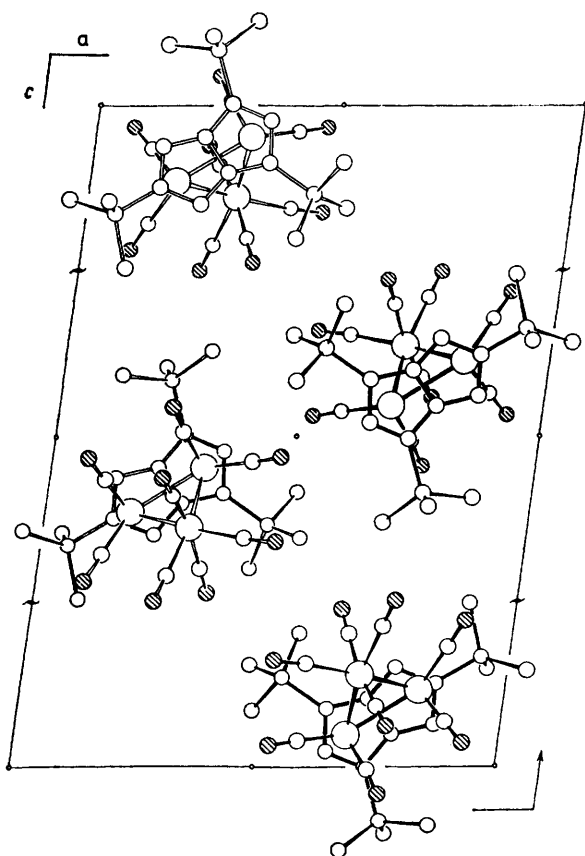


FIGURE 3 Contents of the monoclinic unit cell of edge-bonded isomer (A), viewed in projection down  $b$  looking towards the origin

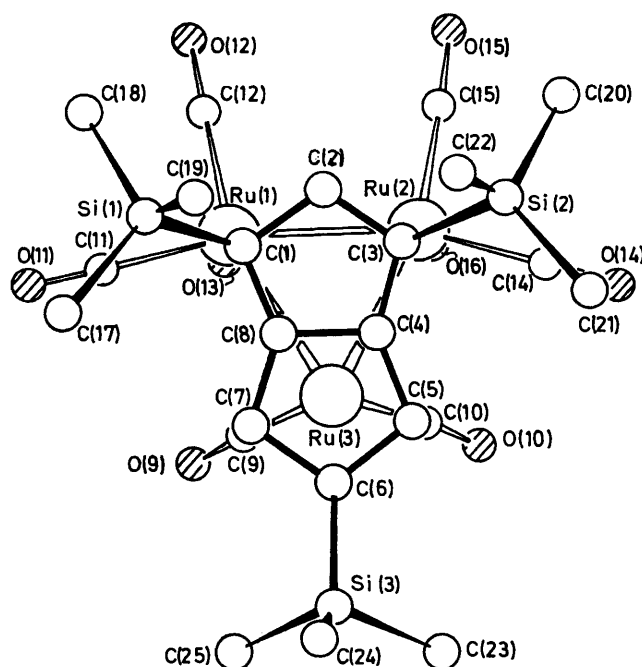


FIGURE 4 Molecular structure of the face-bonded isomer (B) of  $[\text{Ru}_3(\text{CO})_9\{\text{C}_8\text{H}_8(\text{SiMe}_3)_3-1,3,5\}]$ , viewed perpendicular to the plane of the pentalene moiety, and showing the crystallographic numbering sequence

the corresponding values are  $2.21$  and  $2.53$  Å, all with estimated standard deviations (e.s.d.s) of *ca.*  $0.02$ . Despite the shorter Ru-Ru bond in the  $\text{Ru}_3$  complex, however, the pentalene is still non-planar; the two  $\text{C}_5$  rings hinge (Table 3) at an interplanar angle of  $171^\circ$  ( $173^\circ$  in the  $\text{Ru}_2$  complex). The hinge atoms are nearer to the line of the metal-metal bond than are the wingtip atoms.

In the metal-atom triangle Ru(1)-Ru(2) is, within

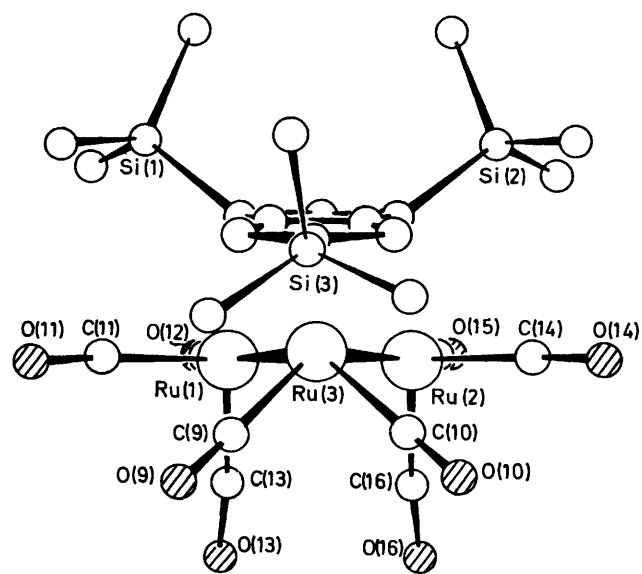


FIGURE 5 Molecular structure of the face-bonded isomer (B) seen along the vector joining the unique ruthenium atom to the midpoint between the other two ruthenium atoms

experimental error, equal to Ru(3)–Ru(2) (mean 2.82 Å). Ru(2), which is not bonded to the pentalene, carries four carbonyl ligands, of which C(10)–O(10) and C(12)–O(12) lie approximately in the plane of the metal triangle (Table 3), while C(9)–O(9) and C(11)–O(11) are axial to it. Ru(1) and Ru(3) each carry two carbonyls: C(13)–O(13) on Ru(1) and C(15)–O(15) on Ru(3) are axial, while C(14)–O(14) on Ru(1) and C(16)–O(16) on Ru(3) are equatorial: all these adopt eclipsed configurations when seen along the Ru(1)–Ru(3) bond as in Figure 2. Furthermore the carbonyls on Ru(1) and Ru(3) appear to have significantly shorter Ru–C, and longer C–O, bonds than those on Ru(2).

2.64 Å from Ru(1) and Ru(2). Atoms C(1), C(3), and C(6) carry the SiMe<sub>3</sub> substituents and, just as in isomer (A), the C–Si bonds deviate sharply from the mean plane of the pentalene away from the Ru<sub>3</sub> triangle (Table 6). The deviation for Si(1) and Si(2) is, however, much greater than that for Si(3) where intramolecular interaction with the CO groups on Ru(3) is much reduced by the bending of these two CO ligands away from the plane of the pentalene (Figure 5). Again the two C<sub>5</sub> rings of the pentalene are not quite coplanar (interplanar angle 174°, see Table 6), but here the trend is in the reverse direction *i.e.*, the bridge atoms are further from the Ru<sub>3</sub> plane than are the wingtips. Ru(1) and Ru(2) each

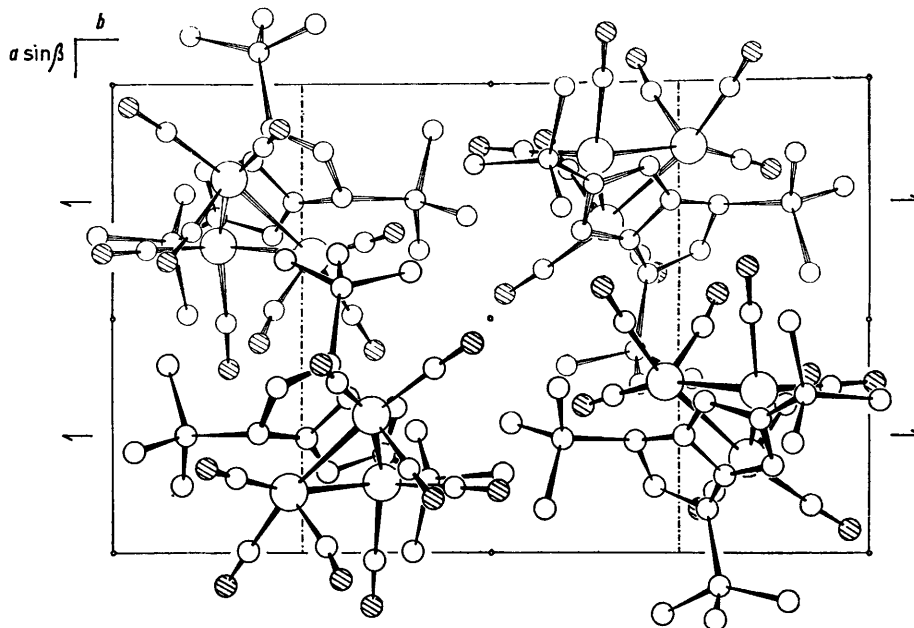


FIGURE 6 Contents of the monoclinic cell of face-bonded isomer (B), viewed in projection down  $c$  looking towards the origin

The three SiMe<sub>3</sub> groups are linked to the pentalene nucleus by bonds which deviate significantly from the plane of the C<sub>5</sub> ring to which they are attached (Table 3), in a direction away from the metal triangle. The bonds around the Si atoms do not appear to deviate from a regular tetrahedral arrangement in any systematic way. The packing of the molecules within the monoclinic unit cell is shown in Figure 3.

The face-bonded isomer (B), Figures 4 and 5, is quite different from (A) both in the mode of attachment of the pentalene ligand to the Ru<sub>3</sub> triangle and in the disposition of its carbonyl groups. Again the Ru<sub>3</sub> triangle is isosceles, but now the unique edge Ru(1)–Ru(2) is shorter (2.79 Å) than the other two (mean 2.85 Å). The unique apical atom Ru(3) is  $\eta^5$ -bonded to the mono-substituted C<sub>5</sub> ring C(4)–C(8) at a mean Ru–C bond length of 2.24 Å. The remainder of the pentalene ligand is perhaps best thought of as comprising an inter-annular  $\pi$ -allyl moiety C(1)–C(3) with C(1)  $\sigma$ -bonded to Ru(1) and C(3)  $\sigma$ -bonded to Ru(2) at a mean distance of 2.26 Å; the central atom C(2) is at a mean distance of

carry three carbonyl groups of which two [C(11)–O(11), C(12)–O(12) on Ru(1); C(14)–O(14), C(15)–O(15) on Ru(2)] are equatorial and one [C(13)–O(13) on Ru(1), C(16)–O(16) on Ru(2)] is axial. The packing of the molecules in the monoclinic unit cell is illustrated in Figure 6.

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