Hydrocarbon Complexes of Iron, Ruthenium, and Osmium. Part 12.[1] Triruthenium Complexes of Pentalene derived from Cyclo-octatetraenes and Cyclo-octatrienes

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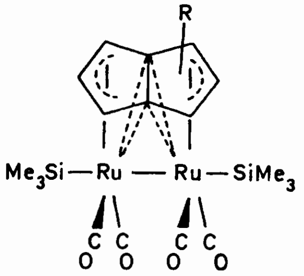
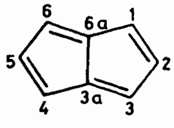
Cyclo-octatetraenes C_8H_7R (R = H, Me, Ph, or $SiMe_3$) and cyclo-octatrienes $C_8H_8(SiMe_3)_2$ and $C_8H_7(SiMe_3)_3$ react with $[Ru_3(CO)_{12}]$ or $[Ru_2(SiMe_3)_2(CO)_8]$ to give, among other products, triruthenium pentalene compounds $[Ru_3(CO)_8(\text{pentalene})]$. Complexes containing unsubstituted or symmetrically substituted pentalene exist as two isomers in which the hydrocarbon is either edge- or face-bonded with respect to an Ru_3 triangle. Hydrogen-1 n.m.r. studies establish that in solution these isomers are in equilibrium, with the predominant edge-bonded form also undergoing an oscillatory fluxional process. The combined effect of these processes is to achieve migration of the pentalene ligand over the faces and edges of the triruthenium cluster. Unsymmetrically substituted pentalene complexes exist exclusively as edge-bonded isomers which do not undergo dynamic behaviour. Trifluoroacetic acid readily cleaves trimethylsilyl groups from complexed pentalene, but other attempted electrophilic substitution reactions have been unsuccessful, as were attempts to isolate pentalenes or pentalene dimers by oxidation of the complexes. Treatment of $[Ru_3(CO)_8\{C_8H_3(SiMe_3)_3\text{-}1,3,5\}]$ with H_2 (1 atm) gave a tetraruthenium complex $[Ru_4H_2(CO)_9\{C_8H_3(SiMe_3)_3\}]$.

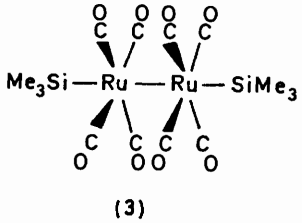
We described earlier[1] the ability of the complex $[Ru(SiMe_3)_2(CO)_4]$ to induce dehydrogenative ring closure of cyclo-octatetraene or substituted cyclo-octatetraenes C_8H_7R (R = H, Me, Ph, or $SiMe_3$) to yield diruthenium complexes $[Ru_2(SiMe_3)_2(CO)_4(C_8H_5R)]$ (1) containing the unstable hydrocarbon pentalene (2) or its derivatives. The relationship between the structures of $[Ru_2(SiMe_3)_2(CO)_8]$[2,3] (3) and of the complexes (1)[4] led naturally to an investigation of the reactions of the former species with cyclo-octatetraenes. We now report that complex (3) and also $[Ru_3(CO)_{12}]$, effect ring closure of cyclo-octatetraenes and trimethylsilyl-substituted cyclo-octatrienes, to produce in each case triruthenium complexes of general formula $[Ru_3(CO)_8(\text{pentalene})]$. This approach to pentalene synthesis has been reviewed[5] and various aspects of the work have been briefly reported.[6-8]



(1)



(2)



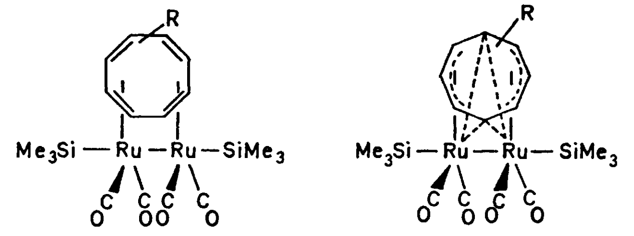
(3)

RESULTS AND DISCUSSION

Reactions of Cyclo-octatetraenes.—The reaction of cyclo-octatetraene (cot) with complex (3) proceeds smoothly in hexane at reflux to afford $[Ru_2(SiMe_3)_2(CO)_4(C_8H_8)]$ (4) exclusively and in high yield, derived apparently by direct substitution of carbonyl ligands across the metal–metal bond. In heptane or octane at reflux (4) is formed in lesser amount but is still the major product. Also produced under these conditions are low yields of three related pentalene complexes $[Ru_3(CO)_8(C_8H_6)]$ (5), $[Ru_3(CO)_8\{C_8H_5(SiMe_3)\text{-}1\}]$ (6), and $[Ru_3(CO)_8\{C_8H_5(SiMe_3)\text{-}2\}]$ (7). Treatment of (3) with the monosubstituted cyclo-octatetraenes C_8H_7R (R = Me, Ph, or $SiMe_3$) gave analogous products $[Ru_2(SiMe_3)_2(CO)_4(C_8H_7R)]$ (8)—(10), $[Ru_3(CO)_8(C_8H_5R\text{-}1)]$ (6), (11), (12), $[Ru_3(CO)_8(C_8H_5R\text{-}2)]$ (7), (13), (14), as well as disubstituted pentalene complexes $[Ru_3(CO)_8\{C_8H_4(R\text{-}1)(SiMe_3\text{-}5)\}]$ (15)—(17).

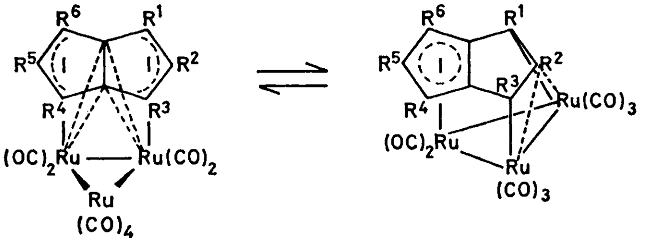
The migration of $SiMe_3$ groups from ruthenium to a co-ordinated pentalene is in accord with previous studies[1,9,10] on the reactions of unsaturated hydrocarbons with trimethylsilyl(carbonyl)ruthenium complexes. Formation of trimethylsilyl-substituted pentalene complexes appears to be particularly favoured, in that the reaction of $C_8H_7(SiMe_3)$ with (3) in octane gave $[Ru_3(CO)_8\{C_8H_5(SiMe_3)\}]$ (6) and (7) and $[Ru_3(CO)_8\{C_8H_4(SiMe_3)_2\text{-}1,5\}]$ (17) in 15 and 35% yields, respectively. The other pentalene complexes were obtained in less than 10% yield.

The formation of the various carbonylruthenium pentalene complexes, devoid of metal-bound $SiMe_3$ groups, suggested that $[Ru_3(CO)_{12}]$ itself might afford such species. This was found to be the case. A re-investigation of the reaction of cot with $[Ru_3(CO)_{12}]$ led to the identification of two new complexes, formed in low yield (1—3%), in addition to the several characterised previously.[11-13] One of these, a tetrahydropentalenyl complex of formula $[Ru_3(CO)_6(\eta^5\text{-}C_8H_9)(\eta^7\text{-}C_8H_9)]$ (18) has been the subject of an *X*-ray diffraction study by Bau *et al.*[14] The other proved to be the pentalene complex (5). The substituted cyclo-octatetraenes C_8H_7R (R = $SiMe_3$ or Ph) react similarly with $[Ru_3(CO)_{12}]$ in heptane or octane to give, respectively, (6), (7), (12), and (14), but in very low yield.



(a) (b)

	R
(4)	H
(8)	Me
(9)	Ph
(10)	SiMe3



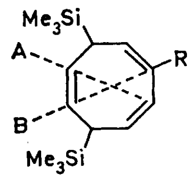
(a) (b)

	R1	R2	R3	R4	R5	R6
(5)	H	H	H	H	H	H
(6)	SiMe3	H	H	H	H	H
(7)	H	SiMe3	H	H	H	H
(11)	Me	H	H	H	H	H
(12)	Ph	H	H	H	H	H
(13)	H	Me	H	H	H	H
(14)	H	Ph	H	H	H	H
(15)	Me	H	H	H	SiMe3	H
(16)	Ph	H	H	H	SiMe3	H
(17)	SiMe3	H	H	H	SiMe3	H
(27)	SiMe3	H	SiMe3	H	SiMe3	H

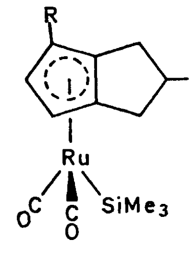
There are three different dehydrogenative ring-closure paths by which a pentalene molecule could be generated from a cyclo-octatetraene C_8H_7R. No evidence has been obtained for a 1,5-closure with R-group ejection; *i.e.* no complexes of unsubstituted pentalene are formed on reaction of C_8H_7R (R = Me, Ph, or $SiMe_3$) with (3) or $[Ru_3(CO)_{12}]$. No strong preference is shown for the other two paths, involving 2,6- or 3,7-closure. Less $[Ru_3(CO)_8(C_8H_5R\text{-}1)]$ is formed than $[Ru_3(CO)_8(C_8H_5R\text{-}2)]$ when R = Me or Ph, with the reverse being the case for R = $SiMe_3$. This may indicate that electron-withdrawing substituents favour 3,7-*trans*-annular ring closure and formation of 2-substituted isomers, but the yields of the complexes are in general less than 10% and firm conclusions are unwarranted.

Reactions of Cyclo-octatrienes.—The results of the experiments outlined above indicated that the formation of pentalene complexes was favoured by the presence of trimethylsilyl substituents in the C_8 ring. This was confirmed through experiments involving reactions of 5,8-bis(trimethylsilyl)cyclo-octa-1,3,6-triene (19)[15,16] and 2,5,8-tris(trimethylsilyl)cyclo-octa-1,3,6-triene (20) with either (3) or $[Ru_3(CO)_{12}]$. The reaction of unsubstituted cyclo-octatriene with (3) produces[17] the complexes $[Ru(SiMe_3)(CO)_2(C_8H_9)]$ (21), $[Ru(CO)_3(C_8H_{10})]$ (22), and $[Ru_2(CO)_6(C_8H_{10})]$ (23), the last two products being more readily obtained directly from $[Ru_3(CO)_{12}]$. A ring closure to give the pentalene carbon skeleton is evident in (21), but dehydrogenation has been sufficient to form only the η^5-tetrahydropentalenyl ligand. Both cyclo-octatrienes (19) and (20) are, however, more extensively dehydrogenated by either (3) or $[Ru_3(CO)_{12}]$ and provide pentalene complexes in low to moderate yields.

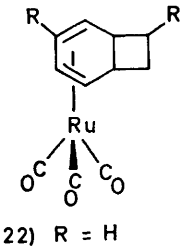
Treatment of the disubstituted cyclo-octa-1,3,6-triene (19) with (3) or $[Ru_3(CO)_{12}]$ in heptane at reflux gives the bis(trimethylsilyl)pentalene complex (17) in 5—10% yield in addition to (24) and (25), and also (26) when (3) is the ruthenium source. The reaction products from trisubstituted (20) with (3) or $[Ru_3(CO)_{12}]$ differ. The tris(trimethylsilyl)pentalene complex $[Ru_3(CO)_8\{C_8H_3(SiMe_3)_3\text{-}1,3,5\}]$ (27) is obtained in 10% yield upon heating (20) with $[Ru_3(CO)_{12}]$ in heptane. Complexes (6) and (7) are also formed in *ca.* 4% combined yield. The formation of pentalene complexes resulting from $SiMe_3$ group loss is more extreme on reaction of (20) with (3), when no tris(trimethylsilyl)pentalene complex is formed at all; the products are (17) (7%) and both isomers (6) and (7) of $[Ru_3(CO)_8\{C_8H_5(SiMe_3)\}]$ (3%). The tris(trimethylsilyl)-substituted analogues of (21)—(23) were



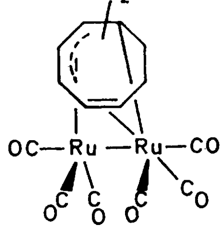
(19) R = H
(20) R = SiMe3



(21) R = H
(26) R = SiMe3



(22) R = H
(24) R = SiMe3



(23) R = H
(25) R = SiMe3

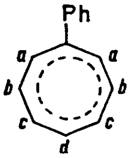
also formed in these reactions but no effort was made to characterise them fully.

In the reaction of the substituted cyclo-octatrienes with $[Ru_3(CO)_{12}]$ the dominant ring-closure pathway, as revealed by the products, is that designated A on (19) and (20). Reaction of (20) with complex (3) proceeds such that ring closure B is favoured, with elimination of $SiMe_3$, for reasons which are not apparent.

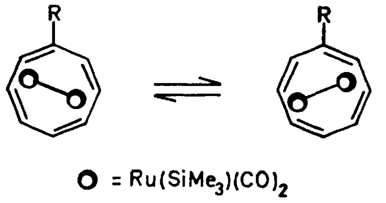
Reactions of 5,8-bis(trimethylgermyl)-2-(trimethylsilyl)cyclo-octa-1,3,6-triene and 5,8-bis(t-butyl)cyclo-octa-1,3,6-triene with (3) and $[Ru_3(CO)_{12}]$ gave only traces of i.r.-detected pentalene complexes. Evidently the $SiMe_3$ group has a unique ability in fostering pentalene complex formation.

Complexes $[Ru_2(SiMe_3)_2(CO)_4(C_8H_7R)]$.—The complexes $[Ru_2(SiMe_3)_2(CO)_4(C_8H_7R)]$ (4), (8), (9), and (10) are air- and solution-stable, yellow, and crystalline. Their i.r. spectra display two strong and two weak terminal carbonyl bands in a pattern very similar to that of the pentalene complex (1). The mass spectra show prominent molecular ions and competitive loss of methyl and CO groups on fragmentation. The ^1H n.m.r. spectrum of the unsubstituted complex (4) consists of two singlets [τ 5.5 (8 H), 9.5 (18 H)] which are unchanged from −150 °C [CCl_2FH-$CClF_2H$ (1 : 1) solution] to 30 °C, in accord with the cot ligand undergoing a very low-energy fluxional rotation. The two plausible ground-state molecular structures (4a) and (4b) are based on the established structures of $[Mn_2(CO)_6(\mu\text{-}C_8H_8)]$[18] and $[Fe_2(CO)_5(\mu\text{-}C_8H_8)]$,[19] respectively. Since it has not been possible to record an n.m.r. spectrum of the rigid molecule we cannot assign firmly one or the other. Moreover, while the close structural similarity of the metal-containing fragments of (4) and $[Mn_2(CO)_6(\mu\text{-}C_8H_8)]$ might favour the 1,3-diene bonding mode, the equally close similarity of the i.r. spectra of (4) and (1) favours the allylic mode.

The seven cot-ring protons of the substituted complexes (8)—(10) appear as a group of overlapping signals in the ^1H n.m.r. spectrum. The spectrum of (9) alone is readily analysed; it displays a doublet [τ 4.80 (2 H)] and three triplets [τ 5.39 (2 H), 5.57 (2 H), 5.62 (1 H)] assigned as a result of double-irradiation experiments to the protons at *a*, *c*, *b*, and *d* respectively. Only a single $SiMe_3$-group signal is observed. Clearly, the molecule adopts either a structure in which the C_8H_7Ph ligand is symmetrically bound to the metal-containing fragment or is undergoing a fluxional process such that a mirror plane is generated bisecting the ligand through the carbon atom bearing the phenyl group.



N.m.r. spectra obtained at −30 and −60 °C in CCl_3F solution showed changes in the shifts of the cot-ring protons of (9) (signals due to *a*, *c*, and *d* moved downfield, and *b* upfield) which did not continue on further cooling to −90 °C. However, there were no indications of signal broadening typical of a slowing down of fluxional motion. Changes in the spectra of (8) and (10) are also observed at low temperatures but could not be defined clearly. In view of the very rapid fluxionality of (4) we believe that the monosubstituted analogues are most likely also fluxional, but the dynamic process within these species may be more oscillatory than rotational in character, *viz.* Scheme 1.



SCHEME 1

The characterisation of complexes (21)—(26) was straightforward and based on i.r., n.m.r., and mass spectra (Tables 1 and 2). N.m.r. spectra reveal that each complex exists as a single isomer, which in turn indicates that specific ring closure of (19) has occurred in the formation of (24) and (26), with accompanying hydrogen shifts. The n.m.r. spectrum of (25) has four ring protons of substantially aliphatic and four of olefinic character, allowing four possible dispositions of the two 1,4-related $SiMe_3$ groups.

Pentalene Complexes.—The pentalene complexes discovered in this investigation are of general formula $[Ru_3(CO)_8(\text{pentalene})]$, obtained as yellow-orange crystals, stable in air at room temperature apparently indefinitely, and for several days in solution. Purification was by chromatography on silica gel or alumina, a technique which also allowed efficient separation of 1- and 2-substituted isomers of $[Ru_3(CO)_8(C_8H_5R)]$. Each complex has a mass spectrum showing a molecular ion followed by loss of eight carbonyl groups. Further characterisation was achieved by i.r. and ^1H n.m.r. spectroscopy (Table 1) and through four single-crystal *X*-ray diffraction studies.[6-8] The complexes fall into two classes: those containing pentalenes substituted unsymmetrically, and those substituted symmetrically, with respect to a plane perpendicular to the plane of the pentalene and passing through C(2) and C(5).

Unsymmetrical complexes. The complexes of this type are of the form $[Ru_3(CO)_8(C_8H_5R\text{-}1)]$ (R = Ph or $SiMe_3$) and $[Ru_3(CO)_8\{C_8H_4(R\text{-}1)(SiMe_3\text{-}5)\}]$ (R = Me, Ph, or $SiMe_3$). The i.r. spectra exhibit eight carbonyl bands, all terminal, in a pattern similar to that shown in Figure 1(*a*). An *X*-ray diffraction study[7,20] of $[Ru_3(CO)_8\{C_8H_4(SiMe_3)_2\text{-}1,5\}]$ (17) has shown that this complex has a structure (17a) with an edge-bridging pentalene ligand. From this result it may be inferred that complexes (6), (11), (12), (15), and (16) have similar structures, existing as the isomers (a), so that the substituted pentalene ligands are co-ordinated to two ruthenium

TABLE 1

Spectroscopic properties of the complexes

	Complex	ν(CO) [a]/cm^{-1}	^{1}H N.m.r. (τ) [b]
(4)	$[Ru_2(SiMe_3)_2(CO)_4(C_8H_8)]$	2 026s, 2 019w (sh), 1 986w, 1 971s	[c] 5.5 (s, 8 H), 9.5 (s, 18 H)
(8)	$[Ru_2(SiMe_3)_2(CO)_4(C_8H_7Me)]$	2 028s, 2 022w (sh), 1 991w, 1 973s	[d] 5.4 (t, 2 H, *J* 7), 5.8 (m, 5 H), 7.9 (s, 3 H), 9.6 (s, 18 H)
(9)	$[Ru_2(SiMe_3)_2(CO)_4(C_8H_7Ph)]$	2 028vs, 2 022w (sh), 1 991w, 1 974s	2.7 (m, 5 H), 4.84 (d, 2 H, *J* 9), 5.29 (t, 2 H, *J* 8.3), 5.57 (t, 2 H, *J* 8.7), 5.62 (t, 1 H, *J* 8), 9.6 (s, 18 H)
(10)	$[Ru_2(SiMe_3)_2(CO)_4\{C_8H_7(SiMe_3)\}]$	2 031s, 2 025w (sh), 1 996w, 1 978s	5.2 (m, 7 H), 9.2 (s, 18 H), 9.3 (s, 9 H)
(5a)	$[Ru_3(CO)_8(C_8H_6)]$	2 089s, 2 029s, 2 015vs, 2 008s, 2 000w, 1 987w, 1 962m, 1 950w	[e] 3.8 (t, 2 H, *J* 2.5), 6.2 (d, 4 H, *J* 2.5); [f] 3.7 (t, 2 H, *J* 2.5), 5.4 (d, 2 H, *J* 2.5), 6.9 (d, 2 H, *J* 2.5)
(5b)		[g] 2 077, 2 040	4.0 (t, 1 H, *J* 3), 4.5 (t, 1 H, *J* 2), 5.0 (d, 2 H, *J* 3), 5.5 (d, 2 H, *J* 2)
(6a)	$[Ru_3(CO)_8\{C_8H_5(SiMe_3)\text{-}1\}]$	2 085s, 2 028s, 2 013vs, 2 005s, 1 995w, 1 983w, 1 957m, 1 943w	4.0 (m, 2 H), 5.7 (d, 1 H, *J* 2), 7.0 (d, 2 H, *J* 2), 10.0 (s, 9 H)
(7a)	$[Ru_3(CO)_8\{C_8H_5(SiMe_3)\text{-}2\}]$	2 087s, 2 028s, 2 012vs, 2 005s, 1 997w, 1 982w, 1 957m, 1 944w	[e] 3.8 (t, 1 H, *J* 2.5), 6.3 (d, 2 H, *J* 2.5), 6.4 (s, 2 H), 9.6 (s, 9 H); [f] 3.7 (t, 1 H, *J* 2.5), 5.4 (d, 1 H, *J* 2.5), 5.7 (s, 1 H), 7.0 (d, 1 H, *J* 2.5), 7.1 (s, 1 H), 9.6 (s, 9 H)
(7b)		[g] 2 073, 2 042	4.0 (t, 1 H, *J* 2.5), 5.0 (d, 2 H, *J* 2.5), 5.7 (s, 2 H), 9.8 (s, 9 H)
(12a)	$[Ru_3(CO)_8(C_8H_5Ph\text{-}1)]$	2 087s, 2 029s, 2 015vs, 2 007s, 1 998w, 1 987w, 1 962m, 1 949w	2.8 (m, 5 H), 3.3 (d, 1 H, *J* 2), 3.7 (t, 1 H, *J* 2.5), 5.2 (d, 1 H, *J* 2.5), 6.8 (d, 1 H, *J* 2), 6.9 (d, 1 H, *J* 2.5)
(13a)	$[Ru_3(CO)_8(C_8H_5Me\text{-}2)]$	2 086s, 2 027s, 2 012vs, 2 005s, 1 996w, 1 985w, 1 959m, 1 946w	4.1 (t, 1 H, *J* 2.5), 6.4 (s, 2 H), 6.5 (d, 2 H, *J* 2.5), 7.6 (s, 3 H); [f] 4.1 (t, 1 H, *J* 2.5), 5.7 (s, 1 H), 5.8 (d, 1 H, *J* 2.5), 7.2 (s, 1 H), 7.3 (d, 1 H, *J* 2.5), 7.6 (s, 3 H)
(13b)		[g] 2 074, 2 038	[h] 4.5 (1 H), 5.7 (2 H), 5.9 (2 H), 7.9 (s, 3 H)
(14a)	$[Ru_3(CO)_8(C_8H_5Ph\text{-}2)]$	2 088s, 2 029s, 2 016w, 2 008s, 1 998w, 1 988w, 1 962m, 1 949w	[e] 2.5 (m, 5 H), 3.8 (t, 1 H, *J* 2.5), 5.6 (s, 2 H), 6.1 (d, 2 H, *J* 2.5); [f] 2.5 (m, 5 H), 3.8 (t, 1 H, *J* 2.5), 4.9 (s, 1 H), 5.4 (d, 1 H, *J* 2.5), 6.4 (s, 1 H), 6.9 (d, 1 H, *J* 2.5)
(14b)		[g] 2 076, 2 042	[g,h] 4.8 (s, 2 H), 5.2 (2 H)
(15a)	$[Ru_3(CO)_8\{C_8H_4(Me\text{-}1)(SiMe_3\text{-}5)\}]$	2 086s, 2 027s, 2 013vs, 2 005s, 1 997w, 1 984w, 1 956m, 1 934w	3.8 (d, 1 H, *J* 2.5), 5.7 (s, 1 H), 7.1 (s, 1 H), 7.2 (d, 1 H, *J* 2.5), 8.1 (s, 3 H), 9.7 (s, 9 H)
(16a)	$[Ru_3(CO)_8\{C_8H_4(Ph\text{-}1)(SiMe_3\text{-}5)\}]$	2 086s, 2 028s, 2 014vs, 2 006s, 1 997m, 1985w, 1 958m, 1 945w	2.8 (m, 5 H), 3.3 (d, 1 H, *J* 2.5), 5.4 (s, 1 H), 6.9 (d, 1 H, *J* 2.5), 7.0 (s, 1 H), 9.6 (s, 9 H)
(17a)	$[Ru_3(CO)_8\{C_8H_4(SiMe_3)_2\text{-}1,5\}]$	2 085s, 2 026s, 2 010vs, 2 003s, 1 995w (sh), 1 981w, 1 953m, 1 940w	3.8 (d, 1 H, *J* 2.5), 5.8 (s, 1 H), 6.9 (d, 1 H, *J* 2.5), 7.0 (s, 1 H), 9.6 (s, 9 H), 10.0 (s, 9 H)
(24)	$[Ru(CO)_3\{C_8H_8(SiMe_3)_2\}]$	2 058s, 1 994s, 1 984s	4.6 (d of dd, 1 H, *J* 7, 1.5, 0.7), 6.3 (d of d, 1 H, *J* 7, 4.5), 6.5 (d of d, 1 H, *J* 4.5, 1.5), 7.6 (m, 2 H), 8.4 (m, 1 H), 8.8 (m, 1 H), 9.4 (m, 1 H), 9.7 (s, 18 H)
(25)	$[Ru_2(CO)_6\{C_8H_8(SiMe_3)_2\}]$	[i] 2 070s, 2 060 (sh), 2 035s, 2 005s, 1 990m, 1 979m, 1 975m	5.4 (m, 2 H), 5.8 (m, 2 H), 8.2 (m, 4 H), 9.7 (s, 9 H), 9.9 (s, 9 H)
(26)	$[Ru(SiMe_3)(CO)_2\{C_8H_7(SiMe_3)_2\}]$	[i] 2 004s, 1 946s	5.0 (d, 1 H, *J* 3), 5.3 (d, 1 H, *J* 3), 7.3 (m, 4 H), 7.8 (m, 1 H), 9.6 (s, 9 H), 9.7 (s, 9 H), 9.9 (s, 9 H)
(27a)	$[Ru_3(CO)_8\{C_8H_3(SiMe_3)_3\text{-}1,3,5\}]$	2 087s, 2 028m, 2 012vs, 2 002s, 1 996w, 1 984w, 1 954m, 1 943w	[d] 4.0 (s, 1 H), 6.5 (s, 2 H), 9.6 (s, 9 H), 9.9 (s, 18 H); [j] 4.0 (s, 1 H), 5.9 (s, br, 1 H), 7.2 (s, br, 1 H), 9.6 (s, 9 H), 9.9 (s, 18 H)
(27b)		2 072s, 2 037s, 2 001s, 1 993m, 1 975w, 1 969w, 1 943w	[d] 4.5 (s, 1 H), 5.9 (s, 2 H), 9.7 (s, 18 H), 9.8 (s, 9 H)
(30)	$[Ru_4H_2(CO)_9\{C_8H_3(SiMe_3)_3\text{-}1,3,5\}]$	2 077s, 2 048s, 2 011vs, 1 999m, 1 981m, 1 964m, 1 940w,br, 1 892w,br	4.4 (s, 1 H), 6.3 (s, 2 H), 9.6 (s, 9 H), 9.8 (s, 18 H), 27.3 (s, 2 H)
(31)	$[Ru(SiMe_3)(CO)_2\{C_8H_7(SiMe_3)_2\}]$	2 019s, 1 945s	5.2 (s, 1 H), 5.3 (s, 1 H), 7.9 (m, 5 H), 9.8 (s, 9 H), 10.0 (s, 9 H), 10.2 (s, 9 H)
(32)	$[Ru(SiMe_3)(CO)_2\{C_8H_6(SiMe_3)_3\}]$	2 006s, 1 949bs	5.0 (s, 2 H), 7.8 (m, 4 H), 9.7 (s, 9 H), 9.9 (s, 18 H), 10.0 (s, 9 H)

[a] In hexane solution unless otherwise stated. [b] In $CDCl_3$ solution unless otherwise stated. Coupling constants in Hz. [c] In benzene solution. [d] In CCl_3F solution. [e] Measured at 60 °C. [f] Measured at −60 °C. [g] Other bands obscured by corresponding bands of isomer (a). [h] Bands very weak, minor isomer. [i] In cyclohexane solution. [j] In CCl_3F solution at −100 °C.

atoms of an Ru_3 isosceles triangle in a manner similar to that within the diruthenium pentalene complex (1).[4] Thus, as with (1), the ruthenium–carbon(ring) distances in (17a) fall into two groups, the 'allylic' carbons being at a mean distance of 2.23 Å and the 'bridging' carbons at 2.48 Å. The most significant feature of the structure is that the plane of the metal triangle makes a 50° angle with the mean plane of the pentalene ligand. This angle is close to that expected if the complex is envisaged as being derived from $[Ru_3(CO)_{12}]$ through the pentalene replacing an axial and an equatorial carbonyl ligand on each of a pair of ruthenium atoms. The two trimethylsilyl substituents are in the 1- and 5-positions, with the plane of the Ru_3 triangle leaning away from the 1-substituent. This is presumably a steric effect, and leads to the presumption that in (6a), (11a), (12a), (15a), and (16a) a similar situation arises.

The positions of substitution in related pentalene complexes are readily deduced from their ^{1}H n.m.r. spectra. For example, the spectrum of (12a) has been shown by double-irradiation experiments to comprise a coupled set of a triplet (τ 3.7) and two doublets (τ 5.2, 6.9) due to the unsubstituted five-membered ring, and another coupled set of two doublets (τ 3.3, 6.8) clearly due to a 1-substituted ring. In addition, the n.m.r. spectra of (15a)—(17a) are each consistent with 1,5-disubstitution, showing a coupled pair of doublets and two singlet signals for the four ring protons. Assignment of the trimethylsilyl substituent of (15a) and (16a) to the 5-position, and the Me or Ph group to the 1-position, is made by comparing their spectra with those of (11a), (12a), and (17a). The shifts and fine structures of the ring-proton signals are characteristic.

None of these complexes having unsymmetrically substituted pentalene ligands shows any temperature dependence of their n.m.r. spectra, *i.e.* they are probably non-fluxional.

Symmetrical complexes. The complexes in this class are of the form $[Ru_3(CO)_8(C_8H_5R\text{-}2)]$ (R = H, Me, Ph, or $SiMe_3$) and $[Ru_3(CO)_8\{C_8H_3(SiMe_3)_3\text{-}1,3,5\}]$. These display the same thermal- and air-stability as complexes of unsymmetrical pentalenes, and are also yellow-orange and crystalline. However, both i.r. and ^1H n.m.r. spectra reveal that the complexes exist as two isomers. Crystallisation of $[Ru_3(CO)_8\{C_8H_3(SiMe_3)_3\text{-}1,3,5\}]$ (27) from hexane affords two kinds of crystal: yellow and orange-red prisms, respectively, which may be hand-separated. The yellow form has an i.r. spectrum [Figure 1(*a*)] analogous to those of the unsymmetrically substituted pentalene complexes discussed above, while the spectrum of the orange-red isomer is quite different [Figure 1(*b*)]. Upon crystallisation of the $[Ru_3(CO)_8(C_8H_5R\text{-}2)]$ complexes only the yellow form is isolable in a pure state.

TABLE 2

Physical and analytical data for new ruthenium complexes [a]

	Complex	Colour	M.p. (θ_c/°C) (decomp.)	Analysis (%) C	Analysis (%) H	*M* [b]
(4)	$[Ru_2(SiMe_3)_2(CO)_4(C_8H_8)]$	Yellow	203	38.5 (38.3)	4.7 (4.6)	564 (564)
(5)	$[Ru_3(CO)_8(C_8H_6)]$	Orange	220	30.6 (30.5)	1.0 (1.0)	631 (631)
(6)	$[Ru_3(CO)_8\{C_8H_5(SiMe_3)\text{-}1\}]$	Orange	160	32.1 (32.5)	2.1 (2.0)	703 (703)
(7)	$[Ru_3(CO)_8\{C_8H_5(SiMe_3)\text{-}2\}]$	Orange	160	32.4 (32.5)	2.1 (2.0)	703 (703)
(9)	$[Ru_2(SiMe_3)_2(CO)_4(C_8H_7Ph)]$	Yellow	151	45.0 (45.0)	4.7 (4.7)	641 (641)
(10)	$[Ru_2(SiMe_3)_2(CO)_4\{C_8H_7(SiMe_3)\}]$	Yellow	90			637 (637)
(12)	$[Ru_3(CO)_8(C_8H_5Ph\text{-}1)]$	Orange	166	37.9 (37.5)	1.8 (1.4)	707 (707)
(13)	$[Ru_3(CO)_8(C_8H_5Me\text{-}2)]$	Orange	192	31.7 (31.6)	1.2(1.2)	645 (645)
(14)	$[Ru_3(CO)_8(C_8H_5Ph\text{-}2)]$	Orange	216	37.7 (37.5)	1.4 (1.4)	707 (707)
(16)	$[Ru_3(CO)_8\{C_8H_4(Ph\text{-}1)(SiMe_3\text{-}5)\}]$	Yellow	189	39.0 (38.6)	2.4 (2.3)	779 (779)
(17)	$[Ru_3(CO)_8\{C_8H_4(SiMe_3)_2\text{-}1,5\}]$	Yellow	125	34.7 (34.1)	3.2 (2.9)	775 (775)
(24)	$[Ru(CO)_3\{C_8H_8(SiMe_3)_2\}]$	White	55—57 [c]	47.1 (46.9)	6.0 (6.0)	436 (436)
(25)	$[Ru_2(CO)_6\{C_8H_8(SiMe_3)_2\}]$	Yellow	130—132	38.6 (38.7)	4.2 (4.2)	621 (621)
(27)	$[Ru_3(CO)_8\{C_8H_3(SiMe_3)_3\text{-}1,3,5\}]$	Orange	135	35.7 (35.5)	3.8 (3.6)	847 (847)

[a] Calculated values are given in parentheses. [b] Molecular weight by mass spectrometry. [c] Melts without decomposition.

X-Ray diffraction studies [8,21] were performed on each isomer of $[Ru_3(CO)_8\{C_8H_3(SiMe_3)_3\text{-}1,3,5\}]$. These established that the major, yellow isomer was indeed of structure (27a), *i.e.* containing an edge-bonded pentalene ligand inclined at an angle of 51° to the Ru_3 plane, a result similar to that found for (17a). The minor, orange-red isomer has both a different mode of attachment of the pentalene and a different distribution of carbonyl groups, but is also based on an Ru_3 triangle. The structure is best represented as (27b), in which the pentalene lies almost parallel to and effectively spans a face of the Ru_3 triangle. The hydrocarbon is η^5-bonded to one ruthenium and σ-bonded to each of the other two [Ru–C 2.26(3) Å] which are 'bridged' by the remaining carbon [Ru–C 2.64(2) Å]. The interaction of this second ring with the two ruthenium atoms could perhaps be described as a 'bridging allyl.' Although the silicon in the 5-position of the pentalene is effectively coplanar with the mean C_8 plane, the other two are *ca.* 1 Å out of this plane away from the ruthenium triangle, in keeping with considerable sp^3 character for the ring carbons to which they are attached.

An *X*-ray diffraction study [6,20] of the yellow isomer of the unsubstituted pentalene complex $[Ru_3(CO)_8(C_8H_6)]$ also revealed a structure (5a) with features similar to those of (17a) and (27a). As mentioned earlier, the face-bonded forms (b) of the complexes $[Ru_3(CO)_8(C_8H_5R\text{-}2)]$ (R = H, Me, Ph, or $SiMe_3$) were not isolable. It seems likely, however, that in view of the structure of (27b) the 5-substituent is present in the η^5- rather than the η^3-bonded ring.

If a solution of either isomer of $[Ru_3(CO)_8\{C_8H_3(SiMe_3)_3\text{-}1,3,5\}]$ (27) is allowed to stand at room temperature for several minutes, i.r. bands due to the other isomer appear and ultimately an equilibrium mixture is achieved with the edge-bonded isomer (27a) predominating [Figure 1(*c*)]. This i.r. spectrum is typical of those obtained for the other isomeric mixtures. The relative intensities of the bands due to each isomer vary with the nature of the pentalene, and for each complex a substantial increase in the proportion of face-bonded isomer (b) is observed when spectra of warm solutions are recorded. These indications that the isomeric edge- and face-bonded pentalene complexes are in equilibrium in solution are confirmed by ^1H n.m.r. studies.

The ^1H n.m.r. spectra of the $Ru_3(CO)_8$ complexes [(7), (13), (14), and (27)] of symmetrically substituted pentalenes, and of pentalene itself (5), exhibit two sets of resonances which can be attributed to isomers of the form (a) and (b). The variation in the relative intensi-

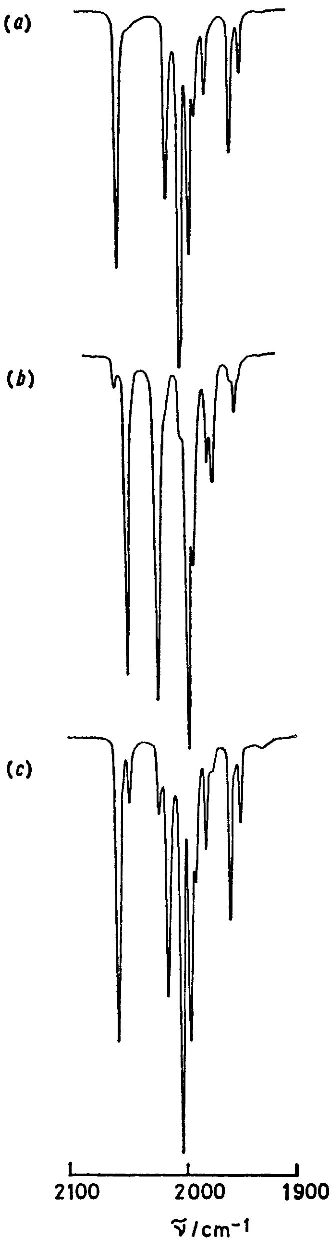


FIGURE 1 Infrared spectra (in hexane) in the carbonyl-stretching region for $[Ru_3(CO)_8\{C_8H_3(SiMe_3)_3\text{-}1,3,5\}]$ (27): (*a*) isomer (27a), (*b*) isomer (27b), and (*c*) equilibrium mixture of these two isomers

ties of these two sets with temperature clearly establishes that the two isomers are in equilibrium. Moreover, the predominant set of resonances, due to isomer (a), shows changes with temperature characteristic of fluxional motion. The spectrum of $[Ru_3(CO)_8\{C_8H_5(SiMe_3)\text{-}2\}]$ (7) at various temperatures is typical and is presented in Figure 2. Almost identical behaviour is shown by (5) and the analogous complexes $[Ru_3(CO)_8(C_8H_5R\text{-}2)]$ [(13) and (14)], but for $[Ru_3(CO)_8\{C_8H_3(SiMe_3)_3\text{-}1,3,5\}]$ the limiting high-temperature spectrum of isomer (27a) is observed at ambient temperature. In this case coalescence is achieved at *ca.* −75 °C and even at −100 °C the spectrum shows the consequences of fluxional motion.

Consideration of the −63 °C spectrum of $[Ru_3(CO)_8\text{-}\{C_8H_5(SiMe_3)\text{-}2\}]$ (7) (Figure 2) in association with Scheme 2 leads to the three signals of relative intensity 1 : 2 : 2, designated *a*—*e*, being attributed to the five ring protons of the face-bonded isomer (7b). Resonance *a* is the expected triplet, as a result of coupling to the equivalent pair *b*–*c*, which appears as a doublet. Protons *d*–*e*, also equivalent, occur as the expected singlet. The set of resonances *A*–*E* due to protons of the predominant edge-bonded isomer (7a) is more complex since the symmetry is lowered as a result of the Ru_3 triangle making a 50° angle with the pentalene. Protons *B*—*E*

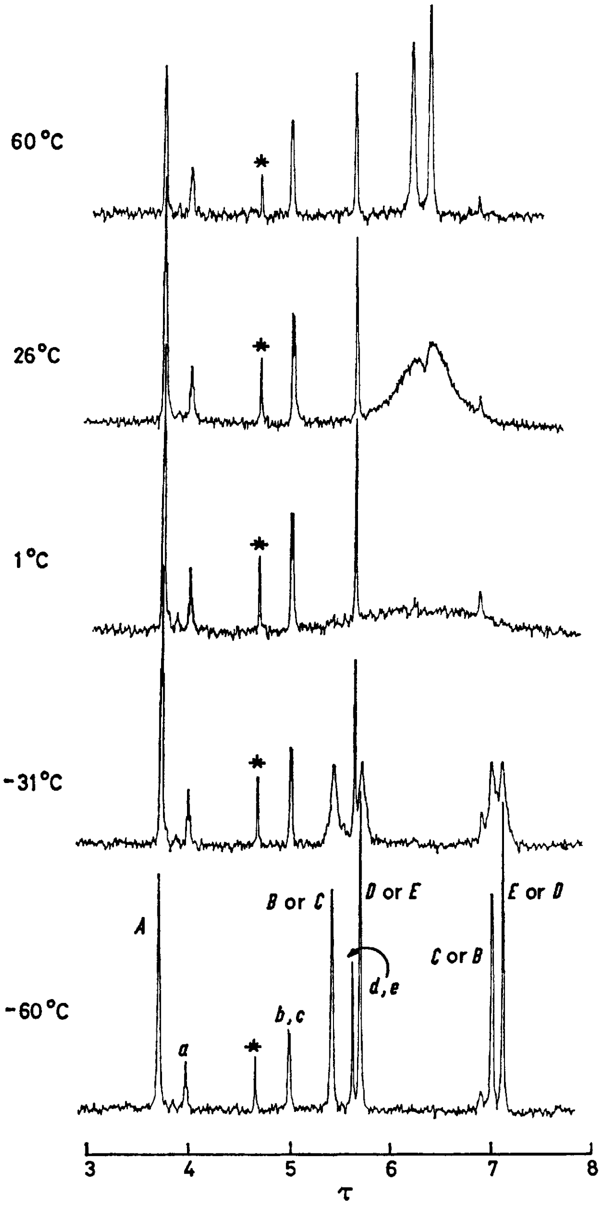
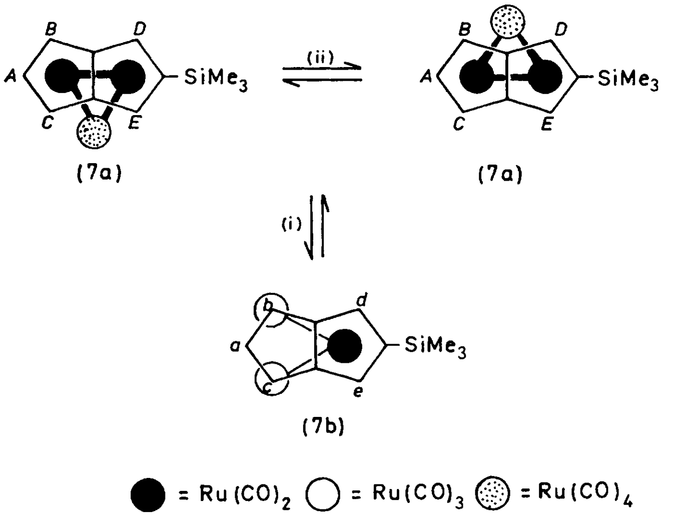


FIGURE 2 Hydrogen-1 n.m.r. spectrum (220 MHz) of $[Ru_3\text{-}(CO)_8\{C_8H_5(SiMe_3)\text{-}2\}]$ (7) in $CDCl_3$. The asterisk indicates resonance of CH_2Cl_2

are thus non-equivalent. Although individual assignment of *B*–*E* is not possible, the *B*–*C* and *D*–*E* pairs are clearly indicated by their small and zero coupling to *A*, respectively.

The spectrum of the face-bonded isomer (7b) does not vary with temperature. However, that of edge-bonded (7a) varies such that on warming site *B* is averaged with *C*, and *D* with *E*, *i.e.* a time-averaged mirror plane is generated which passes through the $SiMe_3$ substituent and *A*, whose n.m.r. signal is thus unaffected. We propose that this arises *via* the oscillatory fluxional process (ii) shown in Scheme 2. This may be seen either as a movement of the pentalene about one edge of the Ru_3 triangle, or as a pendulum-like swing of the $Ru(CO)_4$ group with respect to the hydrocarbon.

The free energy of activation of this oscillation, calculated as 12.4 ± 0.3 kcal mol^{-1} for $[Ru_3(CO)_8\{C_8H_5(SiMe_3)\text{-}2\}]$ (7a) and 12.8 ± 0.3 kcal mol^{-1} for the analogous complexes $[Ru_3(CO)_8(C_8H_5R\text{-}2)]$ (5a), (13a), and (14a), is rather insensitive to the nature of the 2-substituent. However, for trisubstituted $[Ru_3(CO)_8\{C_8H_3(SiMe_3)_3\text{-}1,3,5\}]$ (27a) $\Delta G^{\ddagger}$ is considerably lower at 9.2 ± 0.2 kcal mol^{-1}.* This may be a steric effect, in that the 1,3-disubstitution could be envisaged to destabilise the ground-state structure relative to a transitional one in which the Ru_3 triangle and pentalene are orthogonal.



SCHEME 2

The non-fluxionality of the unsymmetrically substituted pentalene complexes (6a), (11a), (12a), (15a), (16a), and (17a) may be traced to the fact that an oscillation of type (ii) within these would generate an isomer of unequal rather than, as in Scheme 2, equal free energy. In principle an interconversion of such isomers could still occur. If this was the case, however, one would expect the n.m.r. spectra to show some variation in chemical shifts or broadening of signals on cooling to the temperatures (−60 to −100 °C) at which the symmetrical pentalene complexes become static.

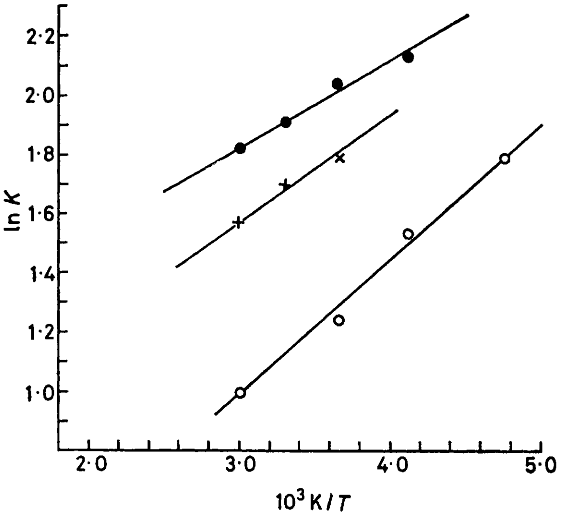
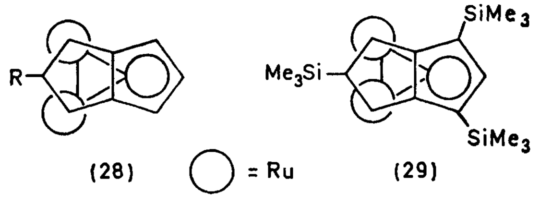


FIGURE 3 Temperature dependence of the equilibrium between isomers (a) and (b) of $[Ru_3(CO)_8\{C_8H_3(SiMe_3)_3\text{-}1,3,5\}]$ (27) (●), $[Ru_3(CO)_8(C_8H_6)]$ (5) (×), and $[Ru_3(CO)_8\{C_8H_5(SiMe_3)\text{-}2\}]$ (7) (○)

The variation with temperature of the equilibrium constant between the isomers (a) and (b) was measured from the ^1H n.m.r. spectra of $[Ru_3(CO)_8(C_8H_6)]$ (5), $[Ru_3(CO)_8\{C_8H_5(SiMe_3)\text{-}2\}]$ (7), and $[Ru_3(CO)_8\{C_8H_3(SiMe_3)_3\text{-}1,3,5\}]$ (27). This allowed the construction of plots of ln *K versus* T^{-1} (Figure 3), from which the standard changes in enthalpy and entropy for the isomerisation (a) $\rightleftharpoons$ (b) were calculated as follows: (5), $\Delta H^{\ominus} = 0.7 \pm 0.1$ kcal mol^{-1} and $\Delta S^{\ominus} = -1.0 \pm 0.3$ cal K^{-1} mol^{-1}; (7), $\Delta H^{\ominus} = 0.6 \pm 0.1$ kcal mol^{-1} and $\Delta S^{\ominus} = -2.0 \pm 0.3$ cal K^{-1} mol^{-1}; (27) $\Delta H^{\ominus} = 0.9 \pm 0.1$ kcal mol^{-1} and $\Delta S^{\ominus} = 0.7 \pm 0.3$ cal K^{-1} mol^{-1}.

These isomerisations [process (i) of Scheme 2] are remarkable in requiring the shift of a hydrocarbon ligand from the edge of a metal cluster to a face and *vice versa*, with simultaneous carbonyl migration between ruthenium atoms. Moreover, as presented in Scheme 3, for (5) a combination of (i) edge $\rightleftharpoons$ face isomerisation and (ii) fluxional oscillation of the edge isomer allows the migration of the pentalene over *all* the faces and edges of the cluster. Identical behaviour by the substituted pentalene complexes $[Ru_3(CO)_8(C_8H_5R\text{-}2)]$ (R = Me, Ph, or $SiMe_3$) and $[Ru_3(CO)_8\{C_8H_3(SiMe_3)_3\text{-}1,3,5\}]$ would require the existence of a second face-bonded isomer, *e.g.* (28) or (29). There is no n.m.r. spectral evidence for the existence of such species, suggesting that a more limited motion of these pentalenes is likely (Scheme 4).



Recently, attention has been drawn to the importance of ‘steps,’ ‘kinks,’ and ‘terraces’ on a metal surface

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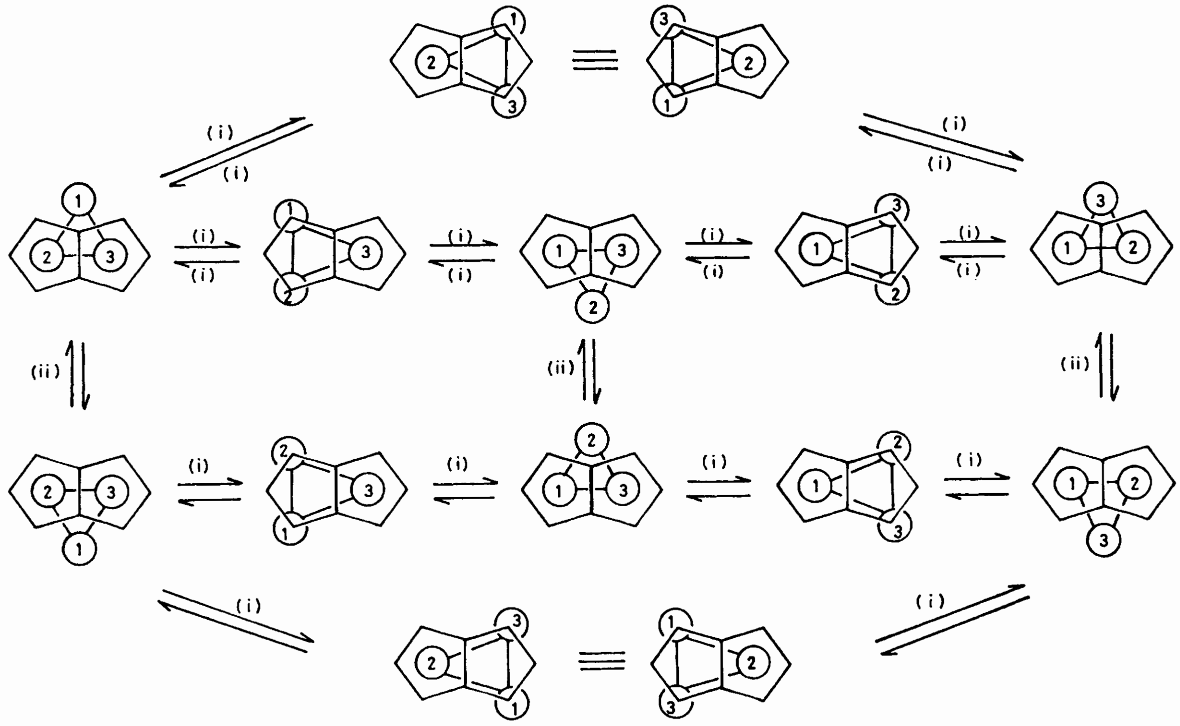
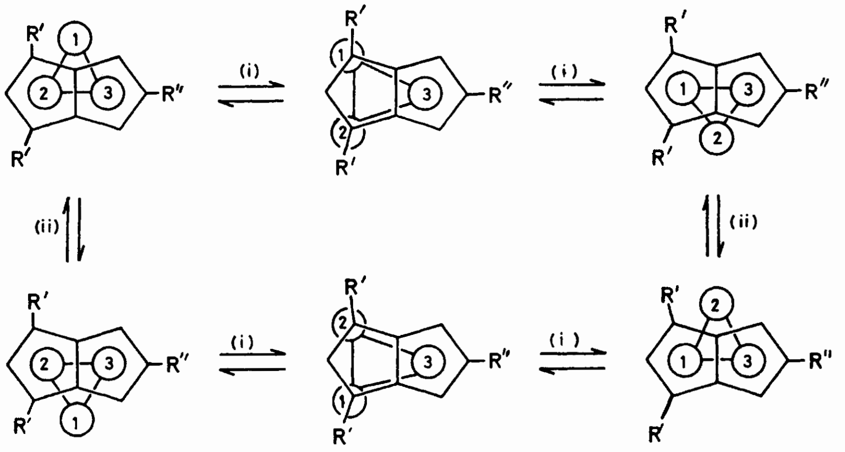
* Throughout this paper: 1 cal = 4.184 J; 1 mmHg ≈ 13.6 × 9.8 Pa; 1 atm = 101 325 Pa.

involved in catalysis.[22] The mobility of a polyolefin on such a surface may have features related to the behaviour described here.



Scheme 3 Process (i) and process (ii) as in Scheme 2

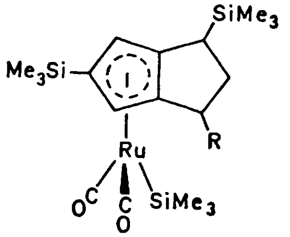


Scheme 4 R′ = R″ = $SiMe_3$, or R′ = H, R″ = Me, Ph, or $SiMe_3$

Reactions. Attempts to separate the pentalene ligands from the triruthenium cluster by oxidative reagents were unsuccessful. The problems associated with isolating either a very unstable pentalene or its dimer were compounded by the necessity of working with small amounts of metal complex, of which the major portion is the carbonylmetal moiety. From the reaction of $[Ru_3(CO)_8\{C_8H_4(SiMe_3)_2\text{-}1,5\}]$ (17a) with $Me_3NO{\cdot}2H_2O$ an unstable green-black organic mixture was isolated, but no identification of its components was achieved. Treatment of (17a) with iodine and (27) with ammonium cerium(IV) nitrate yielded unidentified products still containing carbonyl ligands. This indication of the stability of the complexes is supported by other reactions which reveal that both the pentalene and the ruthenium unit may be modified without destruction of the pentalene-metal link.

Reaction of (27) in octane at reflux with hydrogen at atmospheric pressure affords a polynuclear ruthenium pentalene complex $[Ru_4H_2(CO)_9\{C_8H_3(SiMe_3)_3\text{-}1,3,5\}]$ (30) in good yield, and a trace of spectroscopically identified $[RuH(CO)_2\{C_8H_6(SiMe_3)_3\}]$. The red-black tetraruthenium complex displayed a characteristic mass spectrum, but decomposes slowly even under nitrogen or vacuum and analytical data were not obtained. The ^1H n.m.r. spectrum (Table 1) indicates that the pentalene ligand has remained intact, and also displays a singlet signal at τ 27.3 (2 H) characteristic of hydrogen bridging two ruthenium atoms. The spectrum is unchanged between 35 and −95 °C (CCl_3F solution) so that the evident mirror symmetry of the molecule is most probably real and not generated by a fluxional motion. The i.r. spectrum provides evidence, in a weak absorption at 1 890 cm^{-1}, of semi-bridging carbonyl ligands in the structure. These data do not allow a distinction to be made between structures in which the pentalene is edge- or face-bonded to the Ru_4 cluster. In the former instance a structure derived from that of $[Ru_4H_2(CO)_{13}]$ [23] by simple substitution of four CO ligands by pentalene along one edge could be envisaged. A face-bonded structure may be closely related to that of the 4,6,8-trimethylazulene complex $[Ru_4(CO)_9(C_{10}H_5Me_3)]$,[24] in which a 10 π-electron face-bonded azulene is replaced by an 8 π-electron pentalene and two bridging hydrido-ligands. Unfortunately, attempts to obtain crystals suitable for an *X*-ray diffraction study were not successful. The reaction of (17a) with hydrogen appeared, in terms of colour changes and i.r. monitoring, to proceed as for the tris(trimethylsilyl)pentalene complex (27), but the product was very unstable and could not be purified.

Treatment of $[Ru_3(CO)_8\{C_8H_4(SiMe_3)_2\text{-}1,5\}]$ (17a) and $[Ru_3(CO)_8\{C_8H_3(SiMe_3)_3\text{-}1,3,5\}]$ (27) with $SiMe_3H$ at 140 °C resulted in the isolation in each case of a single product, the tetrahydropentalenyl complexes (31) and (32) respectively, readily identified spectroscopically (Table 1). It is of interest to note that (31) is isomeric with (26), produced in the reaction of (3) with the cyclo-octatriene (19). These reactions are further evidence of the difficulty of completely removing pentalenes from complexation.



(31) R = H
(32) R = SiMe₃

Desilylation of the pentalene ligand was found to occur when either (6a) or (17a) was treated in dichloromethane solution with CF_3CO_2H, giving the parent complex (5) and the 2-substituted (7), respectively, in good yield. From the latter reaction a trace of $[Ru_3(CO)_8(C_8H_6)]$ (5) was also obtained, but clearly desilylation occurs much more rapidly from the 1- than from the 2(5)-position, *i.e.* the 1-carbon is much more susceptible to electrophilic attack. Trimethylsilyl groups are similarly cleaved from phenyl rings by protic acids. Attempts to achieve acetylation of either (5) or (6a) with $CH_3COCl\text{–}AlCl_3$ were unsuccessful, as were reactions with the nucleophiles MeO^- and Me^-. No reaction occurred with MeO^-, while Me^- effected complete decomposition of the complexes.

EXPERIMENTAL

Techniques and instrumentation were as described in earlier Parts of this Series, except that a Varian Associates HR 220 spectrometer was employed in recording some n.m.r. spectra. The complex $[Ru_2(SiMe_3)_2(CO)_8]$ (3),[2] trimethylsilyl-,[25] phenyl-,[26] and methyl-cyclo-octatetraene [27] and 5,8-bis(trimethylsilyl)cyclo-octa-1,3,6-triene (19) [15,16] were prepared by literature methods. Cyclo-octatetraene was purchased from B.A.S.F., and distilled prior to use.

Free energies of activation of the fluxional processes described were calculated using the relation (1) [28] where

$$\Delta G_{Tc}{}^{\ddagger} = -RT_{\mathrm{o}} \ln (\pi \Delta \nu \boldsymbol{h}/2^{\frac{1}{2}} \boldsymbol{k} T_{\mathrm{c}}) \qquad (1)$$

T_c = coalescence temperature, $\Delta\nu$ = chemical-shift separation of non-exchanging nuclei, and the other symbols have their usual significance. The standard changes in enthalpy and entropy were calculated from the relations (2), *K* and *T* being obtained in variable-temperature n.m.r. studies.

$$\ln (K_2/K_1) = \frac{-\Delta H^{\ominus}}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \text{ and } \ln K = \frac{-\Delta H^{\ominus}}{RT} + \Delta S^{\ominus} \qquad (2)$$

Analytical data and physical and spectroscopic properties of the new complexes are collected in Tables 1 and 2.

Preparation of 2,5,8-*Tris(trimethylsilyl)cyclo-octa*-1,3,6-*triene* (10).—Thin strips of lithium metal (0.7 g, 0.1 mol) were added to a rapidly stirred solution of trimethylsilylcyclo-octatetraene (6.42 g, 0.03 mol) in dry diethyl ether (200 cm^3), and the mixture stirred for 16 h affording a dark brown solution of the dianion $[C_8H_7(SiMe_3)]^{2-}$. This was then added to a stirred diethyl ether (200 cm^3) solution of $SiMe_3Cl$ (9.3 cm^3, 0.07 mol) at −60 °C over 0.5 h. After allowing the mixture to warm to room temperature it was stirred for another 18 h then hydrolysed with water (200 cm^3). The aqueous layer was washed with diethyl ether (50 cm^3) and the combined organic layers washed with water (100 cm^3) before drying over $Mg[SO_4]$. Evaporation of solvent, followed by distillation of the residue, afforded a pale yellow *liquid* $C_8H_7(SiMe_3)_3$ (20) (6.66 g, 57%), b.p. 50—60 °C (10^{-2} mmHg) (Found: C, 63.5; H, 10.0%; *M* 322. $C_{17}H_{34}Si_3$ requires C, 63.3; H, 10.6%; *M* 322); ^1H n.m.r. τ 4.29 (m, 5 H), 7.50 (m, 2 H), 9.94 (s, 9 H), and 9.97 (s, 18 H).

Reactions of $[Ru_2(SiMe_3)_2(CO)_8]$ (3) *with Cyclo-octatetraenes*.—*With* C_8H_8. Complex (3) (0.6 g, 1.1 mmol) and C_8H_8 (0.62 g, 6.0 mmol) were heated in octane (60 cm^3) at reflux for 30 h. Evaporation of solvent and unchanged C_8H_8, followed by chromatography on alumina eluting with hexane, separated $[Ru_2(SiMe_3)_2(CO)_4(C_8H_8)]$ (4) (0.1 g, 16%), $[Ru_3(CO)_8\{C_8H_5(SiMe_3)\text{-}1\}]$ (6a) (5 mg, 1%), $[Ru_3(CO)_8\{C_8H_5(SiMe_3)\text{-}2\}]$ (7) (5 mg, 1%), and $[Ru_3(CO)_8(C_8H_6)]$ (5) (20 mg, 4%), each as yellow-orange *crystals*. Elution with hexane–dichloromethane (2 : 1) developed a broad orange-red band containing a low yield of the known $[Ru_2(CO)_5(C_8H_8)]$ and other unidentified complexes, followed by a red band which yielded 10 mg (2%) of $[Ru_3(CO)_6(C_8H_9)_2]$,[14] each identified by their i.r. and n.m.r. spectra.

From a similar reaction in hexane at reflux (4) was obtained in 67% yield, with only traces of the pentalene complexes being detected.

With $C_8H_7(SiMe_3)$. Complex (3) (1.0 g, 1.8 mmol) and $C_8H_7(SiMe_3)$ (0.32 g, 1.8 mmol) were heated in heptane (200 cm^3) at reflux for 29 h. Chromatography on silica gel, eluting with hexane, gave three yellow-orange bands from which were isolated $[Ru_2(SiMe_3)_2(CO)_4\{C_8H_7(SiMe_3)\}]$ (10) (20 mg, 2%), $[Ru_3(CO)_8\{C_8H_4(SiMe_3)_2\text{-}1,5\}]$ (17a) (0.23 g, 26%), and a mixture (90 mg, 11%) of $[Ru_3(CO)_8\{C_8H_5(SiMe_3)\text{-}1\}]$ (6a) and $[Ru_3(CO)_8\{C_8H_5(SiMe_3)\text{-}2\}]$ (7).

A similar reaction performed in octane (150 cm^3) at reflux for 16 h gave only a trace of (10) but improved yields of (17a) (35%) and of the mixture of $[Ru_3(CO)_8\{C_8H_5(SiMe_3)\}]$ isomers (15%).

With C_8H_7Ph. Complex (3) (0.75 g, 0.87 mmol) and C_8H_7Ph (0.9 g, 5.0 mmol) were heated in heptane (75 cm^3) at reflux for 54 h. Chromatography on alumina, eluting with hexane–dichloromethane (9 : 1), separated in order $[Ru_2(SiMe_3)_2(CO)_4(C_8H_7Ph)]$ (9) (50 mg, 9%), $[Ru_3(CO)_8\{C_8H_4(Ph\text{-}1)(SiMe_3\text{-}5)\}]$ (16a) (5 mg, 1%), $[Ru_3(CO)_8(C_8H_5Ph\text{-}1)]$ (12a) (4 mg, 1%), and $[Ru_3(CO)_8(C_8H_5Ph\text{-}2)]$ (14) (12 mg, 3%).

With C_8H_7Me. Complex (3) (1.1 g, 1.9 mmol) and C_8H_7Me (0.5 g, 4.2 mmol) were heated in heptane (65 cm^3) at reflux for 37 h. Chromatography then gave in order $[Ru_2(SiMe_3)_2(CO)_4(C_8H_7Me)]$ (8) (75 mg, 7%) [contaminated with a small amount of inseparable (4), no analytical data obtained], $[Ru_3(CO)_8\{C_8H_4(Me\text{-}1)(SiMe_3\text{-}5)\}]$ (15a) (5 mg, <1%), $[Ru_3(CO)_8(C_8H_5Me\text{-}1)]$ (11a) (5 mg, <1%), and $[Ru_3(CO)_8(C_8H_5Me\text{-}2)]$ (13) (55 mg, 7%).

Reactions of $[Ru_3(CO)_{12}]$ *with Cyclo-octatetraenes.*—*With* C_8H_8. The complex $[Ru_3(CO)_{12}]$ (0.6 g, 0.93 mmol) and C_8H_8 (0.6 g, 5.8 mmol) were heated in heptane (75 cm^3) at reflux for 24 h. On cooling a substantial quantity of $[Ru_2(CO)_5(C_8H_8)]$ crystallised. Chromatography of the remaining solution on alumina, eluting with hexane, separated several known carbonylruthenium complexes. Thereafter, elution with hexane–dichloromethane (6 : 1) gave yellow, orange, and red bands providing *crystals* of $[Ru_3(CO)_8(C_8H_6)]$ (5) (10 mg, 2%), more $[Ru_2(CO)_5(C_8H_8)]$, and $[Ru_3(CO)_6(C_8H_9)_2]$ (18) (15 mg, 3%) (Found: C, 38.7; H, 2.6%; *M* 683. $C_{22}H_{18}O_6Ru_3$ requires C, 38.8; H, 2.7%; *M* 683), respectively.

With C_8H_7R ($R = Ph$ *or* $SiMe_3$). Reactions performed under similar conditions with C_8H_7R ($R = Ph$ or $SiMe_3$) proceeded similarly to provide very low yields (<1%) of i.r.-identified $[Ru_3(CO)_8(C_8H_5R)]$ upon chromatography. From the reaction with C_8H_7Ph, 25 mg (3%) of red *crystals* of $[Ru_3(CO)_6(C_8H_8Ph)_2]$ (m.p. 213 °C) (Found: C, 48.4; H, 3.2%; *M* 835. $C_{34}H_{26}O_6Ru_3$ requires C, 49.0; H, 3.1%; *M* 835), the phenyl derivative of $[Ru_3(CO)_6(C_8H_9)_2]$ (18), were isolated in addition.

Reactions of $C_8H_8(SiMe_3)_2$ (19).—*With* $[Ru_2(SiMe_3)_2(CO)_8]$ (3). The triene (19) (0.18 g, 0.72 mmol) and complex (3) (0.20 g, 0.35 mmol) were heated in heptane (50 cm^3) at reflux for 7 h. Removal of solvent and chromatography of the residue on silica gel, eluting with hexane, gave in order $[Ru(CO)_3\{C_8H_8(SiMe_3)_2\}]$ (24) (24 mg, 8%), $[Ru(SiMe_3)(CO)_2\{C_8H_7(SiMe_3)_2\}]$ (26) (10 mg, 3%), $[Ru_2(CO)_6\{C_8H_8(SiMe_3)_2\}]$ (25) (18 mg, 6%), and $[Ru_3(CO)_8\{C_8H_4(SiMe_3)_2\text{-}1,5\}]$ (17a) (12 mg, 7%).

With $[Ru_3(CO)_{12}]$. The triene (0.40 g, 1.60 mmol) and $[Ru_3(CO)_{12}]$ (1.0 g, 1.56 mmol) were heated in heptane (150 cm^3) at reflux for 16 h. Treatment of the solution as above then gave compounds (22) (0.72 g, 35%), (21) (0.10 g, 7%), and (17a) (60 mg, 5%).

No pentalene complexes were isolated from similar reactions of (19) with $[Fe_3(CO)_{12}]$ or $[Mn_2(CO)_{10}]$.

Reactions of $C_8H_7(SiMe_3)_3$ (20).—*With* $[Ru_3(CO)_{12}]$. A mixture of $[Ru_3(CO)_{12}]$ (1.0 g, 1.56 mmol) and the triene (20) (1.0 g, 3.1 mmol) was heated in heptane (200 cm^3) at reflux for 16 h. Chromatography as above provided in turn $[Ru_3(CO)_8\{C_8H_3(SiMe_3)_3\text{-}1,3,5\}]$ (27) (0.125 g, 10%) and a mixture of the isomers of $[Ru_3(CO)_8\{C_8H_5(SiMe_3)\}]$ (6a) and (7) (40 mg, 4%). The tris(trimethylsilyl)-substituted analogues of (21)—(23) appeared to be formed in this reaction but no effort was made to purify or characterise these.

With $[Ru_2(SiMe_3)_2(CO)_8]$ (3). The triene (20) (0.3 g, 0.93 mmol) and (3) (0.25 g, 0.48 mmol) were heated in heptane (50 cm^3) at reflux for 19 h. Treatment of the solution as above then gave $[Ru_3(CO)_8\{C_8H_4(SiMe_3)_2\text{-}1,5\}]$ (17a) (15 mg, 7%) and a mixture of the isomers of $[Ru_3(CO)_8\{C_8H_5(SiMe_3)\}]$ (6a) and (7) (6 mg, 3%).

No pentalene complexes were isolated from similar reactions with $[Fe_3(CO)_{12}]$ and $[Mn_2(CO)_{10}]$.

Reactions of Pentalene Complexes.—*With hydrogen.* Hydrogen was bubbled through a solution of $[Ru_3(CO)_8\{C_8H_3(SiMe_3)_3\text{-}1,3,5\}]$ (27) (0.1 g, 0.12 mmol) in octane (100 cm^3) at reflux for 7 h. After evaporation of solvent, the red residue was chromatographed on silica gel, elution with hexane giving a small amount of very unstable white *crystals* formulated as the tetrahydropentalenyl derivative $[RuH(CO)_2\{\eta^5\text{-}C_8H_6(SiMe_3)_3\}]$ on the basis of the i.r. spectrum [ν(CO) at 2 018s, 1 961s cm^{-1}], followed by dark red *crystals* of $[Ru_4H_2(CO)_9\{C_8H_3(SiMe_3)_3\text{-}1,3,5\}]$ (30) (35 mg, 41%).

Similar treatment of $[Ru_3(CO)_8\{C_8H_4(SiMe_3)_2\text{-}1,5\}]$ (17a) with hydrogen yielded only traces of spectroscopically identified $[Ru_4H_4(CO)_{12}]$ upon chromatography.

With $SiMe_3H$. A sealed Pyrex tube containing $[Ru_3(CO)_8\{C_8H_3(SiMe_3)_3\text{-}1,3,5\}]$ (27) (0.11 g, 0.13 mmol) and $SiMe_3H$ (0.5 g, 6.76 mmol) in hexane (50 cm^3) was heated at 140 °C for 24 h. Chromatography, on silica gel eluting with hexane, gave oily yellow *solid* $[Ru(SiMe_3)(CO)_2\{C_8H_6(SiMe_3)_3\}]$ (32) (20 mg, 9%).

Similar treatment of $[Ru_3(CO)_8\{C_8H_4(SiMe_3)_2\text{-}1,5\}]$ (17a) (0.11 g, 0.14 mmol) with $SiMe_3H$ (0.4 g, 5.4 mmol) gave the colourless *oil* $[Ru(SiMe_3)(CO)_2\{C_8H_7(SiMe_3)_2\}]$ (31) (20 mg, 10%), purified by distillation (50° C, 10^{-2} mmHg) onto a water-cooled probe.

With CF_3CO_2H. A sample of $[Ru_3(CO)_8\{C_8H_4(SiMe_3)_2\text{-}1,5\}]$ (17a) (0.16 g, 0.21 mmol) was stirred in a dichloromethane (25 cm^3) solution of CF_3CO_2H (0.2 mol dm^{-3}) at room temperature for 2.5 h. An aqueous solution of Na[OH] (50 cm^3, 0.2 mol dm^{-3}) was then added and the mixture shaken vigorously, resulting in a change in colour of the organic phase from yellow to orange-red. The phases were separated, the water layer washed with dichloromethane (50 cm^3), and the organic phases combined and dried over $Na_2[SO_4]$. Chromatography on silica gel gave unchanged (17a) (45 mg, 28%) and $[Ru_3(CO)_8\{C_8H_5(SiMe_3)\text{-}2\}]$ (7) (65 mg, 45%), identified by i.r. and ^{1}H n.m.r. spectra.

The complex $[Ru_3(CO)_8\{C_8H_5(SiMe_3)\text{-}1\}]$ (6a) (0.39 g, 0.55 mmol), similarly treated, yielded unchanged (6a) (0.22 g, 55%) and $[Ru_3(CO)_8(C_8H_6)]$ (5) (0.13 g, 36%), identified by i.r. and ^{1}H n.m.r. spectra.

With $MeCOCl\text{–}AlCl_3$. The complex $[Ru_3(CO)_8\{C_8H_5(SiMe_3)\text{-}1\}]$ (6a) (0.135 g, 0.19 mmol) and freshly sublimed

$AlCl_3$ (0.23 g, 1.7 mmol) were heated in dichloromethane (50 cm^3) at reflux with MeCOCl (30 mg, 0.4 mmol) for 3 h. The solution was hydrolysed with dilute aqueous Na[OH] then subjected to chromatography on alumina. Elution with hexane gave unchanged (6a) (35 mg, 26%) and (5) (65 mg, 53%). No evidence for acyl-substituted products was obtained in this experiment nor in the similar treatment of (5) with $AlCl_3$–MeCOCl.

With ammonium cerium(IV) *nitrate*. A saturated solution of $[NH_4]_2Ce[NO_3]_6$ in absolute ethanol (40 cm^3) was slowly added to a solution of $[Ru_3(CO)_8\{C_8H_3(SiMe_3)_3\text{-}1,3,5\}]$ (27) (0.1 g, 0.13 mmol) in absolute ethanol (40 cm^3) and the mixture stirred for 0.5 h. Water (100 cm^3) was added, the mixture extracted with diethyl ether (250 cm^3), and the extract dried over $Mg[SO_4]$. Removal of solvent afforded an oily yellow residue which distilled (50 °C, 10^{-1} mmHg) to a water-cooled probe as an unidentified carbonyl-containing species [ν(CO) at 2 055s, 2 011s, 1 735m, and 1 715(sh) cm^{-1}].

With Me_3NO. The complex $[Ru_3(CO)_8\{C_8H_4(SiMe_3)_2\text{-}1,5\}]$ (17a) (0.57 g, 0.73 mmol) and $Me_3NO\cdot2H_2O$ (1 g) were heated in benzene (50 cm^3) at reflux for 1 h. The cooled solution was filtered to remove ruthenium oxide and solvent and NMe_3 evaporated under reduced pressure to leave a green-black organic mixture. Attempts to separate this by crystallisation, vacuum sublimation, or chromatography were unsuccessful.

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