Hydrocarbon Complexes of Iron, Ruthenium, and Osmium. Part 13.[1] The Chemistry of Dicarbonyl(trimethylsilyl)(1—3;6—7-η-8-*endo*-trimethylsilylcyclo-octatrienyl)ruthenium, a Pentalene Precursor

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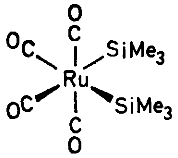
Reactions of $[Ru(SiMe_3)(CO)_2\{1—3;6—7-\ -C_8H_8(8\text{-}endo\text{-}SiMe_3)\}]$ with the compounds $[Ru(SiMe_3)_2(CO)_4]$, $[Ru_2(SiMe_3)_2(CO)_8]$, or $[Ru_3(CO)_{12}]$ give triruthenium pentalene complexes $[Ru_3(CO)_8\{C_8H_{6-n}(SiMe_3)_n\}]$ (n = 0—2). Also formed are two closely related diruthenium complexes $[Ru_2(SiMe_3)(CO)_5(C_8H_8SiMe_3)]$ and $[Ru_2(SiMe_3)(CO)_4(C_8H_8SiMe_3)]$; the former contains a cyclic η^7-C_8 ligand which ring-opens on thermolysis to yield an η^8-C_8 ligand in the latter. Reactions of $[Ru(SiMe_3)(CO)_2\{1—3;6—7\text{-}\eta\text{-}C_8H_7(SiMe_3)_2\text{-}5,8\}]$ with the same reagents give only the pentalene complexes $[Ru_3(CO)_8\{C_8H_{6-n}(SiMe_3)_n\}]$ (n = 0—3), but in increased yields. Heterodimetallic complexes $[FeRu(SiMe_3)(CO)_5(C_8H_8SiMe_3)]$ and $[MnRu(CO)_7(C_8H_7)]$ are obtained on treating $[Ru(SiMe_3)(CO)_2\{1—3;6—7\text{-}\eta\text{-}C_8H_8(8\text{-}endo\text{-}SiMe_3)\}]$ with $[Fe_2(CO)_9]$ or $[MnMe(CO)_5]$, respectively.

IN earlier Parts[1,2] of this Series we described the synthesis of pentalene complexes *via* dehydrogenative *trans*-annular ring closure of cyclo-octatetraenes and cyclo-octatrienes induced by $[Ru(SiMe_3)_2(CO)_4]$ (1), $[Ru_2(SiMe_3)_2(CO)_8]$ (2), or $[Ru_3(CO)_{12}]$. Cyclo-octatetraene or monosubstituted cyclo-octatetraenes C_8H_7R (R = Me, Ph, or $SiMe_3$) were shown to react with (1) in hexane at reflux to afford initially compounds of type (3)[2] (Scheme 1) in which a trimethylsilyl group has migrated to the hydrocarbon ligand. Under more vigorous conditions (heptane or octane at reflux) these same reactions yielded diruthenium pentalene complexes (4) directly, shown to be formed *via* thermolysis of complexes (3). Complexes (2) or $[Ru_3(CO)_{12}]$, on the other hand, reacted with cyclo-octatetraenes or cyclo-octatrienes to give octacarbonyltriruthenium pentalene complexes whose mode of formation is unknown.[1] The established position of (3) as a precursor of (4) led us to study reactions of the former with the carbonylruthenium complexes (1), (2) and $[Ru_3(CO)_{12}]$ with a view to obtaining triruthenium pentalene complexes. These studies are described herein; some aspects have appeared as a preliminary communication.[3]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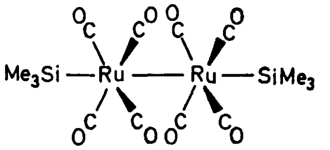
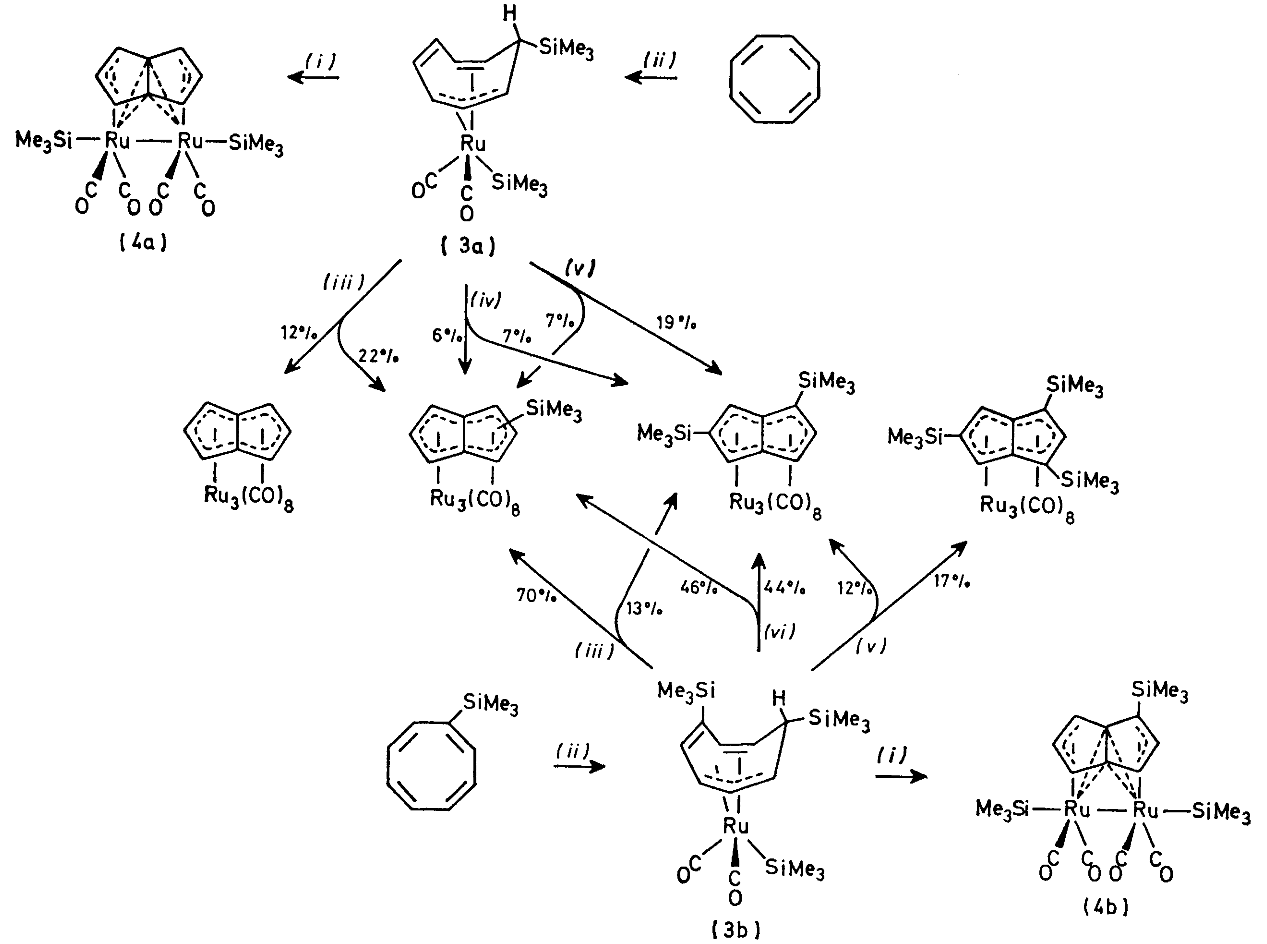

(2)

RESULTS AND DISCUSSION

The results of treating (3a) or (3b)[2] with compounds (1), (2), or $[Ru_3(CO)_{12}]$ are summarised in Scheme 1. In addition to the products of thermolysis [(4a) or (4b)], each complex (3) gave a mixture of triruthenium pentalene complexes (5)—(9) in moderate to good yield, readily separated by chromatography. As described earlier,[1] when the pentalene ligand is unsubstituted or is 2- or 1,3,5-substituted the products are an equilibrium mixture of two isomers (a) and (b), with the pentalene edge- or face-bonded to the triruthenium cluster. In contrast, the unsymmetrical 1- and 1,5-substituted pentalene complexes exist only as the edge-bonded triruthenium species. In each reaction depicted in Scheme 1 two such complexes are formed, whose degree of $SiMe_3$ substitution is clearly dependent upon whether (3a) or (3b) is employed, and upon the number of $SiMe_3$ groups attached to ruthenium in the other reagent. Thus, from (3a) and $[Ru_3(CO)_{12}]$ unsubstituted $[Ru_3(CO)_8(C_8H_6)]$ (5) and monosubstituted $[Ru_3(CO)_8(C_8H_5SiMe_3)]$ are obtained, while at the other extreme (3b) and $[Ru(SiMe_3)_2(CO)_4]$ (1) yield disubstituted $[Ru_3(CO)_8\{C_8H_4(SiMe_3)_2\}]$ (8a) and trisubstituted $[Ru_3(CO)_8\{C_8H_3(SiMe_3)_3\}]$ (9). Both (8a) and (9) are formed as the same isomers obtained by treating (2) with cyclo-octatetraenes and cyclo-octatrienes.[1] However, it is noteworthy that $[Ru_3(CO)_8(C_8H_5SiMe_3)]$ formed from (3a) is a mixture of the 1- and 2-isomers [(6a) and (7), respectively], but that only the 1-isomer is produced from (3b). This parallels the behaviour of (3b) on thermolysis, when 1-substituted $[Ru_2(SiMe_3)_2(CO)_4(C_8H_5SiMe_3)]$ (4b) is formed exclusively. Evidently the specific ring closure[2] of (3b) across C(4)–C(8) upon thermolysis is also favoured in its reactions with carbonylruthenium complexes. The elimination of $SiHMe_3$ noted[2] during thermolysis of (3) was also observed spectroscopically during each of the reactions depicted in Scheme 1.

The reactions of (3a) with (1), (2), or $[Ru_3(CO)_{12}]$ differed from those of (3b) in that two additional products were obtained from (3a), formulated as $[Ru_2(SiMe_3)(CO)_5(C_8H_8SiMe_3)]$ (20—50%) and $[Ru_2(SiMe_3)(CO)_4(C_8H_8SiMe_3)]$ (<5%) on the basis of their mass spectra and analytical data. The i.r. spectrum (Table) of yellow, crystalline, air- and solution-stable $[Ru_2(SiMe_3)(CO)_5(C_8H_8SiMe_3)]$ strongly suggested the structure (10a), the pattern of carbonyl bands being almost identical with those of the compounds $[Ru_2(SiMe_3)(CO)_5(C_7H_6R)]$[4] whose structure (11) has been established by *X*-ray diffraction.[5] The ^1H n.m.r. spectrum (Table) of (10a) is in accord, showing two trimethylsilyl group signals, one having a chemical shift (τ 9.99) character-



SCHEME 1 (*i*) Heating in heptane or octane at reflux, (*ii*) with [Ru(SiMe$_3$)$_2$(CO)$_4$] (1) in refluxing hexane, (*iii*) with [Ru$_3$(CO)$_{12}$] in refluxing octane, (*iv*) with [Ru$_2$(SiMe$_3$)$_2$(CO)$_8$] (2) in refluxing heptane, (*v*) with (1) in refluxing heptane, (*vi*) with (2) in refluxing octane

istic of bonding to carbon and one (τ 9.76) more typical of bonding to ruthenium. In addition, the ring-proton signals appear as five resonances of relative intensity 1 : 2 : 2 : 2 : 1 as expected, with one of these (τ 9.18) clearly aliphatic in character. The assignments given in the Table for (10a) are derived from double-irradiation n.m.r. experiments, as with the other complexes. Decisive evidence in favour of the structure (10a) comes from the similarity of the i.r. and n.m.r. spectra with those of compound (12), obtained from the reaction of [Ru(SiMe$_2$CH$_2$CH$_2$SiMe$_2$)(CO)$_4$] (13) with cyclo-octatetraene,[3,6] and whose structure has been determined by *X*-ray diffraction.[3,7]

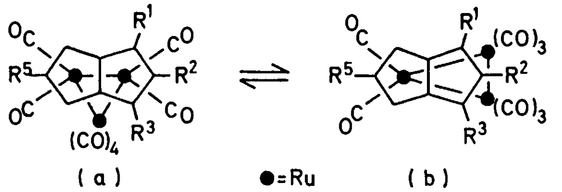
The yellow, crystalline, tetracarbonyldiruthenium

Spectroscopic and physical properties of complexes

	Complex	Colour	(θ_c/°C)	$\tilde{\nu}$(CO) [a]/cm^{-1}	^{1}H n.m.r. (τ) [b]
(10a)	[Ru$_2$(SiMe$_3$)(CO)$_5$(C$_8$H$_8$SiMe$_3$)]	Yellow	154	2 056s, 2 003s, 1 996s, 1 998w (sh), 1 940m	5.42 [1 H, t, *J* 6.5 (H^4)], 6.04 [2 H, dd, *J* 6.5, 7.0 (H^{2,6})], 6.23 [2 H, t, *J* 6.5 (H^{3,5})], 7.69 [2 H, dd, *J* 6, 7 (H^{1,7})], 9.18 [1 H, t, *J* 6 (H^8)], 9.76 (9 H, s), 9.99 (9 H, s)
(10b)	[FeRu(SiMe$_3$)(CO)$_5$(C$_8$H$_8$SiMe$_3$)]	Orange	125 (decomp.)	2 043s, 1 997s, 1 985s, 1 977w (sh), 1 960m	6.00 [1 H, t, *J* 5.5 (H^4)], 6.24 [2 H, t, *J* 5.5 (H^{3,5})], 6.90 [2 H, dd, *J* 7.5, 5.5 (H^{2,6})], 7.48 [2 H, t, *J* 7.5 (H^{1,7})], 9.37 [1 H, t, *J* 7.5 (H^1)], 9.58 (9 H, s), 9.91 (9 H, s)
(14)	[Ru$_2$(SiMe$_3$)(CO)$_4$(C$_8$H$_8$SiMe$_3$)]	Yellow	120	2 033s, 1 995m, 1 976s, 1 957m	1.83 (1 H, d, *J* 9.5), 3.67 (1 H, dd, *J* 9.5, 5), 4.40 (1 H, dd, *J* 5, 6), 4.41 (1 H, dd, *J*, 5, 10), 5.12 (1 H, dd, *J* 6, 7), 7.55 (1 H, dd, *J* 5, 7), 9.32 (1 H, t, *J* 7), 9.50 (1 H, d, *J* 10), 9.62 (9 H, s), 9.83 (9 H, s)
(18)	[MnRu(CO)$_7$(C$_8$H$_7$)]	Yellow	64	2 077m, 1 996vs, 1 983s, 1 968s	3.54 (2 H, AB quartet), 4.62 (1 H, d, *J* 2), 4.90 (1 H, d, *J* 2), 5.05 (1 H, t, *J* 2), 6.79 (2 H, AB quartet)

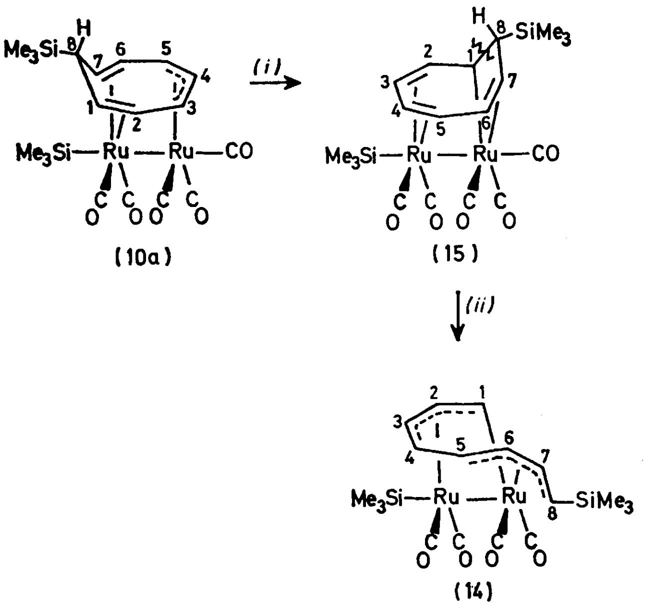
[a] In hexane solutions. [b] In CDCl$_3$ solutions; coupling constants in Hz.

complex $[Ru_2(SiMe_3)(CO)_4(C_8H_8SiMe_3)]$, formed in low yield on treating (3a) with (1), (2), or $[Ru_3(CO)_{12}]$, was evidently derived from (10a) in that heating (10a) in octane at reflux gave the tetracarbonyl in 90% yield. Proton (Table) and ^{13}C [−0.12 (Me_3Si–C), 6.9 (Me_3Si–Ru); 38.3, 42.6, 73.4, 79.7, 96.4, 99.9, 115.4, 148.4 (*C*H); 199.7, 199.9, 202.1, 203.3 (*C*O) p.p.m.] n.m.r. spectra indicated that a substantial rearrangement of the hydrocarbon ligand had occurred, and stimulated the *X*-ray diffraction study described in a succeeding paper.[7] This revealed the structure represented as (14). The spinal Si–Ru–Ru sequence within (10a) has been retained on thermolysis, but the C_8 ring has opened between C(1) and C(8) to form a chain carrying an $SiMe_3$ group on C(8), and with C(1) directly σ-bonded to ruthenium. Atoms C(1)—C(4) are coplanar and form a diene unit η^4-bonded to one ruthenium while C(5)—C(8) are bonded similarly to the other. The length of C(4)–C(5) reveals that the two diene units are independent of one another.



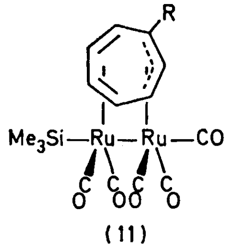
(5) $R^1 = R^2 = R^3 = R^5 = H$
(6) $R^1 = SiMe_3$, $R^2 = R^3 = R^5 = H$
(7) $R^2 = SiMe_3$, $R^1 = R^3 = R^5 = H$
(8) $R^1 = R^5 = SiMe_3$, $R^2 = R^3 = H$
(9) $R^1 = R^3 = R^5 = SiMe_3$, $R^2 = H$

The protons on the terminal carbons of the C_8 chain in (14) resonate at very low (τ 1.83) and very high (τ 9.50) field, but it is not clear to which signal H(1) and H(8) should be assigned. Normally, a degree of carbene character in a carbon atom would cause a low field shift in an attached proton, and for this reason it is likely that H(1) produces the signal at τ 1.83, since C(1) seems most capable of such character. The ^{13}C resonance at 148.4 p.p.m. then becomes assigned to C(1). Areas of shielding and deshielding within the twisted hydrocarbon of (14) are not clearly defined, however, and these assignments remain tentative.

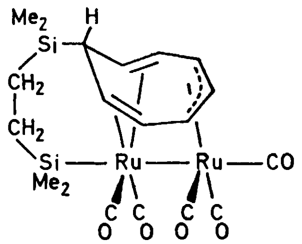


SCHEME 2 (*i*) Isomerisation, (*ii*) —CO

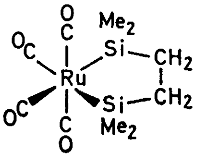
The formation of (14) on thermolysis of (10a) involves an unprecedented C–C bond cleavage to give an unusual open-chain $C_8H_8SiMe_3$ ligand. It is notable that, barring a transfer of the trimethylsilyl group from one carbon to another, the atoms C(1), C(2), and C(5) are the only ones which remain bonded to the same ruthenium in (14) as in (10a). A mechanism consistent with this observation is presented in Scheme 2. In this it is proposed that thermolysis induces a rotation of the hydrocarbon to generate an isomer (15), which satisfies the 18-electron rule. This rearrangement recalls the fact that the related complexes (11) show fluxional motion of the hydrocarbon even at very low (−90 °C) temperatures, although this is not clearly defined. It is suggested that the less favourable co-ordination mode of the hydrocarbon in (15) involves greater ring strain, and that this promotes a C(1)–C(8) bond fission. Twisting about the C(4)–C(5) bond brings the C(5)—C(8) diene unit into co-ordination with elimination of CO. In support of this mechanism, it is significant that complex (12) is stable in octane at reflux, perhaps because the linking of the silicon atoms restricts rotation of the hydrocarbon ligand.



(11)
R = H, Me, Ph, or $SiMe_3$



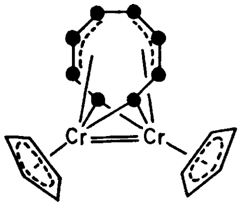
(12)



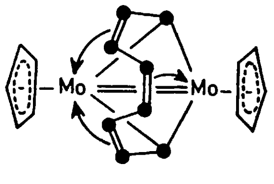
(13)

Very recently the structure of an acyclic C_8 complex of chromium (16) has been described,[8] obtained from disodium cyclo-octatetraenide. Approaching from a different direction, our own studies on the linking of acetylenes at dimetal centres have yielded related species such as (17).[9]

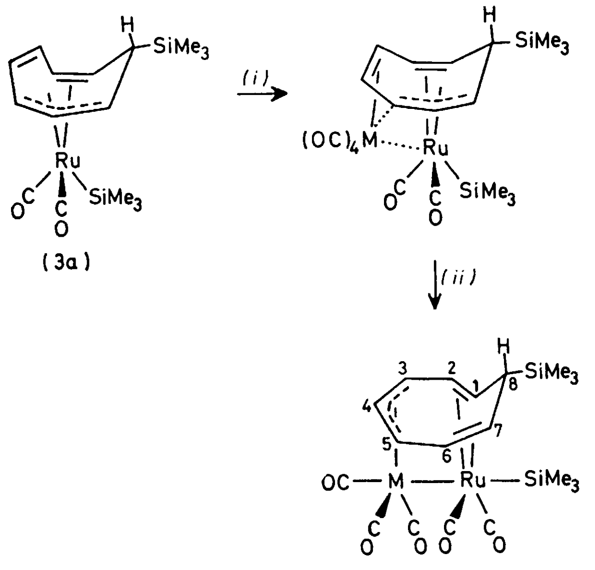
The complex (10a) is derived formally by addition of an $Ru(CO)_3$ fragment to (3a). This suggested that other carbonylmetal groupings, particularly $Fe(CO)_3$, might add similarly. This proved to be the case. The reaction of (3a) with $[Fe_2(CO)_9]$ in hexane at room temperature gave a very high yield of the orange crystalline compound $[FeRu(SiMe_3)(CO)_5(C_8H_8SiMe_3)]$ (10b), whose spectra (Table) were characteristic of a structure analogous to that of (10a). In contrast to (10a), however, the iron complex did not smoothly ring-open on heating; instead, a multitude of low-yield unidentified products was obtained. A credible mechanism for the formation of (10a) and (10b) is displayed in Scheme 3, and envisages the role of compounds (1), (2), $[Ru_3(CO)_{12}]$ or $[Fe_2(CO)_9]$ to be merely sources of '$M(CO)_4$' moieties. The fact that the highest yields of the complexes (10) are obtained from the binary carbonyls supports this view. Moreover, the non-formation of a complex related to (10) on treatment of (3b) with (1), (2) or $[Ru_3(CO)_{12}]$ may be attributed to the steric influence of the $SiMe_3$ substituent on the free double bond acting against coordination of '$Ru(CO)_4$' groups. In view of the scrambling of $SiMe_3$ groups evident from Scheme 1 a simple mechanism for the formation of the triruthenium pentalene complexes is unlikely.



(16) ● = CH

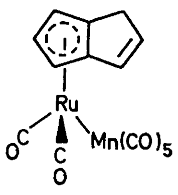


(17) ● = CR



SCHEME 3 (*i*) Addition of $[M(CO)_4]$ (M = Fe or Ru), (*ii*) $-CO$

Treatment of (3a) with $[MnMe(CO)_5]$ gave surprisingly a moderate yield of (10a), but also the heterodimetallic complex $[MnRu(CO)_7(C_8H_7)]$ (18). The mass spectrum of the latter exhibits a molecular ion and immediate fragment ions corresponding to the loss of five carbonyl groups. Thereafter fragmentation follows two paths: (*i*) weak ions are observed due to loss of Mn and then two carbonyl groups, and (*ii*) intense ions due to loss of two carbonyls, then Mn. These data suggest that the two metal atoms and the carbonyls are arranged as an $Mn(CO)_5$ unit and an $Ru(CO)_2$ unit. A medium-intensity ion at *m/e* 103, attributed to $[C_8H_7]^+$, was also observed. The nature of the hydrocarbon as a dihydropentalenyl ligand is evident from the ^1H n.m.r. spectrum (Table). This clearly displays an AB quartet at high field due to the ring methylene group, and an AB quartet at low field due to the adjacent pair of olefinic protons. At intermediate shifts are three signals, two doublets and a triplet, characteristic of the cyclopentadienyl ring protons. A mechanism related to that shown in Scheme 3 could account for the formation of (18), except that elimination of a methyl group from manganese and $SiMe_3$ from ruthenium (as $SiMe_4$ perhaps) is required, followed by ring closure with $SiHMe_3$ ejection.



(18)

EXPERIMENTAL

Infrared spectra were recorded using a Perkin-Elmer 257 spectrometer and n.m.r. spectra using Varian Associates HA100 and HR220 and JEOL PFT-100 instruments. Mass spectra were obtained with an A.E.I. MS902 spectrometer. Reactions were performed under a nitrogen atmosphere with solvents dried by distillation over calcium hydride. Chromatographic separations were on alumina columns (40 × 2 cm) with hexane or light petroleum (b.p. 40—60 °C) as eluant, and products were purified by recrystallisation from hexane–dichloromethane. Complexes (1),[2] (2),[10] and (3)[2] were prepared as previously reported.

Reactions of $[Ru(SiMe_3)(CO)_2(C_8H_8SiMe_3)]$ (3a).—*With* $[Ru(SiMe_3)_2(CO)_4]$ (1). Complexes (1) (0.5 g, 1.4 mmol) and (3a) (0.35 g, 0.87 mmol) were heated in heptane (35 cm^3) under reflux for 16 h. The red-brown solution was cooled, concentrated, and chromatographed, yielding in order: a mixture of (1) and (2), a mixture of (3a) and the tetrahydropentalenyl complex $[Ru(SiMe_3)(CO)_2(C_8H_9)]$,[11] yellow *crystalline* $[Ru_2(SiMe_3)(CO)_4(C_8H_8SiMe_3)]$ (14) (20 mg, 4%) (Found: C, 38.5; H, 4.9%; *M* 565. $C_{18}H_{26}O_4Ru_2Si_2$ requires C, 38.3; H, 4.6%; *M* 565), yellow *crystalline* $[Ru_3(CO)_8\{C_8H_4(SiMe_3)_2\}]$ (8a) (0.13 g, 19%) identified by i.r. and n.m.r. spectroscopy,[1] yellow *crystalline* $[Ru_2(SiMe_3)(CO)_5(C_8H_8SiMe_3)]$ (10a) (0.12 g, 22%) (Found: C, 38.7; H, 4.6%; *M* 593. $C_{19}H_{26}O_5Ru_2Si_2$ requires C, 38.5; H, 4.4%; *M* 593], and finally yellow *crystalline* $[Ru_3(CO)_8(C_8H_5SiMe_3)]$ [isomeric mixture of (6a) and (7)] (40 mg, 7%), identified by i.r. and n.m.r. spectroscopy.[1]

With $[Ru_2(SiMe_3)_2(CO)_8]$ (2). Complexes (2) (0.81 g, 1.41 mmol) and (3a) (0.36 g, 0.80 mmol) were heated in heptane (35 cm^3) under reflux for 17 h. Treatment as above gave unchanged (2) (0.25 g), a trace of $[Ru(SiMe_3)(CO)_2(C_8H_9)]$,[11] (14) (20 mg, 4%), (8a) (50 mg, 7%), (10a) (0.175 g, 33%), and a mixture of (6a) and (7) (40 mg, 6%).

With $[Ru_3(CO)_{12}]$. Complex (3a) (0.44 g, 1.1 mmol) and $[Ru_3(CO)_{12}]$ (0.51 g, 0.8 mmol) were heated in octane (80 cm^3) under reflux for 2.5 h. Treatment as above gave (14) (20 mg, 3%), (10a) (0.37 g, 57%), (6a) (0.125 g, 16%), (7) (50 mg, 6%), and orange *crystalline* $[Ru_3(CO)_8(C_8H_6)]$ (5) (80 mg, 12%), identified by i.r. and n.m.r. spectroscopy.[1]

With $[Fe_2(CO)_9]$. Complex (3a) (1.0 g, 2.5 mmol) and $[Fe_2(CO)_9]$ (2.0 g, 5.5 mmol) were stirred in hexane (50 cm^3) at room temperature for 5 d. Evaporation of solvent and $[Fe(CO)_5]$, followed by chromatography, gave unchanged (3a) (0.5 g) then 0.6 g (88%) of orange *crystalline* $[FeRu(SiMe_3)(CO)_5(C_8H_8SiMe_3)]$ (10b) (Found: C, 41.7; H, 5.1%; *M* 548. $C_{19}H_{26}FeO_5RuSi_2$ requires C, 41.7; H, 4.8% ; *M* 548).

With $[MnMe(CO)_5]$. Complex (3a) (0.49 g, 1.2 mmol) and $[MnMe(CO)_5]$ (0.32 g, 1.5 mmol) were heated in heptane (80 cm^3) under reflux for 11 h. Chromatography gave unchanged (3a) (0.23 g) and a slightly air-sensitive yellow solution which provided 80 mg (20%) of yellow *crystalline* $[MnRu(CO)_7(C_8H_7)]$ (18) (Found: *M* 456. $C_{15}H_7MnO_7Ru$ requires *M* 456), then (10a) (0.125 g, 35%).

Reactions of $[Ru(SiMe_3)(CO)_2\{C_8H_7(SiMe_3)_2\}]$ (3b).—*With* $[Ru(SiMe_3)_2(CO)_4]$ (1). Complexes (3b) (0.48 g, 1.0 mmol) and (1) (1.25 g, 3.5 mmol) were heated in heptane (80 cm^3) under reflux for 48 h. Infrared spectra revealed at this stage that a substantial amount of (4b) was present, but this decomposed on chromatography, which yielded $[Ru_3(CO)_8\{C_8H_3(SiMe_3)_3\}]$ (9) (0.15 g, 17%), (8a) (90 mg, 12%), and a trace of (6a) and (7), each identified by i.r. and n.m.r. spectroscopy.[1]

With $[Ru_2(SiMe_3)_2(CO)_8]$ (2). Compounds (3b) (0.21 g, 0.44 mmol) and (2) (0.3 g, 0.53 mmol) were heated in octane (80 cm^3) under reflux for 3 h. Treatment as above gave unchanged (2) (75 mg), (8a) (0.15 g, 44%), and isomerically pure $[Ru_3(CO)_8(C_8H_5SiMe_3\text{-}1)]$ (6a) (0.14 g, 46%).

With $[Ru_3(CO)_{12}]$. Complex (3b) (0.285 g, 0.59 mmol) and $[Ru_3(CO)_{12}]$ (0.38 g, 0.59 mmol) were heated in octane (80 cm^3) under reflux for 3 h. Treatment as above gave (8a) (60 mg, 13%) and isomerically pure (6a) (0.29 g, 70%), identified by i.r. and n.m.r. spectroscopy.[1]

Thermolysis of $[Ru_2(SiMe_3)(CO)_5(C_8H_8SiMe_3)]$ (10a).—Complex (10a) (0.1 g, 0.17 mmol) was heated in octane (50 cm^3) under reflux for 2 h, after which time i.r. monitoring revealed apparently complete conversion into (14). Chromatography gave a single yellow band which provided 90 mg (90%) of (14), identified by i.r. and n.m.r. spectroscopy.

We thank the S.R.C. for support.

[9/030 *Received, 8th January,* 1979]

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