Hydrocarbon Complexes of Iron, Ruthenium, and Osmium. Part 14.[1] Reactions of a Disilicon-chelated Carbonylruthenium Complex with Cyclic Polyolefins

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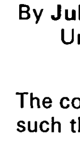
The complex $[\mathrm{Ru(SiMe_2CH_2CH_2SiMe_2)(CO)_4}]$ undergoes reactions with cycloheptatriene and cyclo-octatetraene such that one or both silicon atoms of the chelate ligand migrate to the co-ordinated polyolefin. From C_7H_8 the cycloheptadienyl complex $[\mathrm{Ru(C_7H_8SiMe_2CH_2CH_2SiMe_2)(CO)_2}]$ is produced and converted into the cyclohepta-1,3-diene complex $[\mathrm{Ru(C_7H_8SiMe_2CH_2CH_2SiMe_2)(CO)_3}]$ upon treatment with CO. Similar behaviour is observed using 7-$C_6F_5C_7H_7$. Cyclo-octatetraene yields fully migrated $[\mathrm{Ru(C_8H_8SiMe_2CH_2CH_2SiMe_2)(CO)_3}]$ directly, as well as the diruthenium complex $[\mathrm{Ru_2(C_8H_8SiMe_2CH_2CH_2SiMe_2)(CO)_5}]$ containing an unusual η^7-hydrocarbon ligand bridging the two metal atoms. Cyclopentadiene reacts with $[\mathrm{Ru(SiMe_2CH_2CH_2SiMe_2)(CO)_4}]$ to give a complex $[\mathrm{(OC)_2(\eta\text{-}C_5H_5)RuSiMe_2CH_2CH_2Me_2SiRu(\eta\text{-}C_5H_5)(CO)_2}]$ in which the disilicon chelate links two ruthenium atoms.

In previous Parts [2-5] of this series we have described the reactions of the complexes $[\mathrm{Ru(SiMe_3)_2(CO)_4}]$ (1) and $[\mathrm{Ru_2(SiMe_3)_2(CO)_8}]$ (2) with various cyclic polyolefins. One of the characteristic features of such reactions has been the migration of trimethylsilyl groups from ruthenium to the co-ordinated hydrocarbon. This is exemplified by the formation of complexes (3)—(5) from (1) and cycloheptatriene, cyclo-octatetraene, and azulene respectively, and of complexes (6)—(8) from (2) with cycloheptatriene and cyclo-octatetraene. Such complexes represent a considerable expansion of a field initiated by Gorsich [6,7] with his observation that $[\mathrm{Mn(SnPh_3)(CO)_5}]$ reacts with tetraphenylcyclopentadienone to afford the cymantrene derivative $[\mathrm{Mn\{\eta\text{-}C_5Ph_4(OSnPh_3)\}(CO)_3}]$, a product of migration of the triphenyltin group from manganese to exocyclic oxygen.



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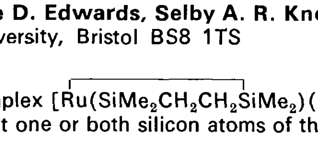

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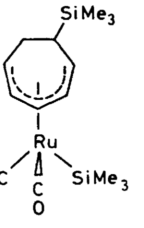

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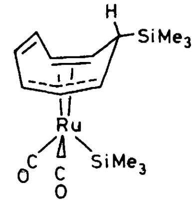

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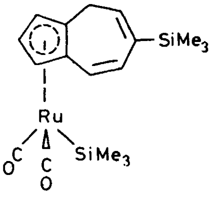

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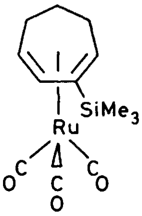
We describe here an extension of our studies to reactions of $[\mathrm{Ru(SiMe_2CH_2CH_2SiMe_2)(CO)_4}]$ (9) [8] with cyclic polyolefins, undertaken with a view to the possibility of migration of one or both ends of the disilicon chelate to a hydrocarbon brought into co-ordination with ruthenium. Aspects of the work have appeared as a preliminary communication.[9]

RESULTS AND DISCUSSION

Reactions with Cycloheptatriene.—The reaction of (9) with cycloheptatriene proceeds readily in heptane under reflux to give white crystalline air- and solution-stable $[\mathrm{Ru(C_7H_8SiMe_2CH_2CH_2SiMe_2)(CO)_2}]$ (10) in high yield (Scheme 1). The mass spectrum of (10) displays a molecular ion and other significant peaks due to the ions $[\mathrm{Ru} - n\mathrm{CO}]^+$ ($n = 1$ or 2), $[\mathrm{Ru - CO - Me}]^+$, $[\mathrm{Ru - 4Me}]^+$, $[\mathrm{Me_2SiCH_2CH_2SiMe_2H}]^+$, and $[\mathrm{C_7H_7}]^+$. In the ^{1}H n.m.r. spectrum there are four singlet signals attributable to methylsilicon protons: two typical of an Me_2Si group bonded only to carbon at τ 9.88 (3 H) and 10.15 (3 H), and two at τ 9.39 (3 H) and 9.55 (3 H) typical of an Me_2Si-Ru fragment, in accord with the migration of one silicon to the C_7 ring while the other remains attached to the metal. A triplet of doublets at τ 3.72 (1 H), two triplets at τ 4.60 (1 H) and 4.79 (1 H), a multiplet at τ 6.28 (1 H), and a doublet of triplets at τ 6.38 (1 H) are characteristic [2] of the 1—5-η-dienyl unit of a cycloheptadienyl ring whose symmetry has been destroyed by substitution at one of the aliphatic carbon atoms. The low-field signal at τ 3.72 is readily assigned to the central dienyl proton H^3 in common with other η^5-dienyl



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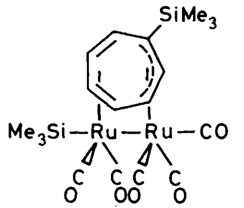

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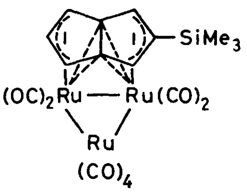
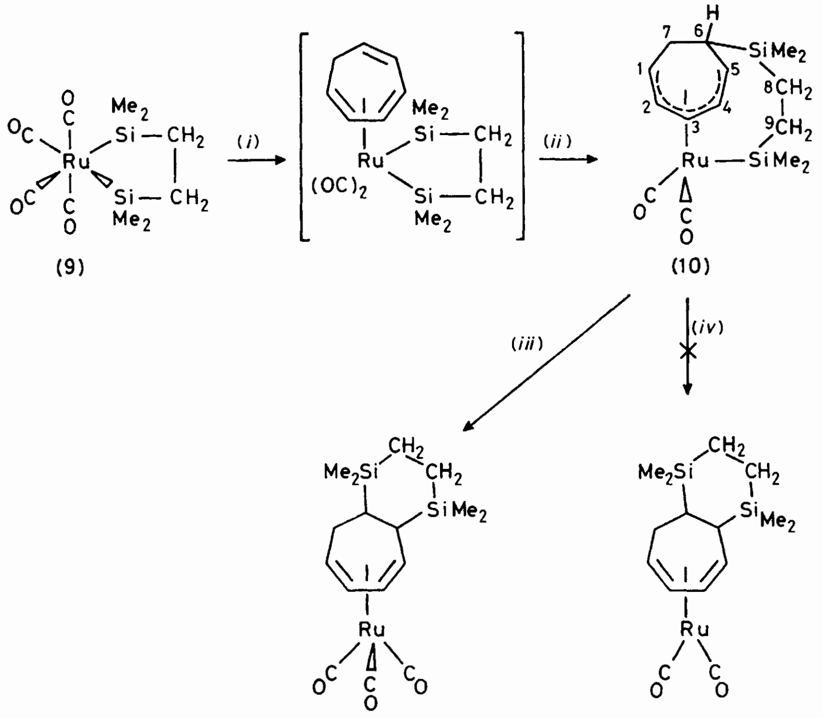


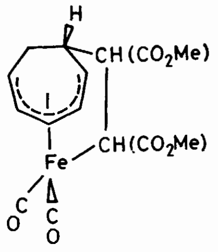
(8)

systems,[2,10] while the two signals close to τ 4.70 are typical of H^2 and H^4. The remaining signals at τ 6.38 and 6.28 are clearly assigned to H^5 and H^1, respectively, on the basis of their multiplicities. A multiplet signal due to the two aliphatic ring protons H^7 appears at τ 7.63 and a broad signal at τ 8.4—9.2 (5 H) is assignable to a combination of substituent chain methylene protons and H^6. Complex (3) exhibits an equally high-field shift for the equivalent proton.[2]



SCHEME 1 (*i*) C_7H_8, $-2CO$; (*ii*) migration; (*iii*) CO; (*iv*) heating. Square brackets indicate postulated complexes, likewise for Schemes 2 and 3

The ^{13}C n.m.r. spectrum confirms the formulation of (10) in having signals at 198.1 and 197.9 p.p.m. (downfield of $SiMe_4$) for two carbonyl groups and ring carbon resonances at 103.1, 101.7, 99.1, 79.4, 74.2, 37.7, and 32.3 p.p.m. Other signals occur at 19.9, 8.7, 7.8, 6.4, —3.7, and —4.6 p.p.m. The high-field pair are of equal intensity and are assigned to the methyl carbons of the $SiMe_2$ group attached to the hydrocarbon ring, as was the case with (3).[2] Resonances at 8.7 and 6.4 p.p.m. are also of comparable intensity and are typical of an $SiMe_2$ group co-ordinated to ruthenium. The remaining signals at 19.9 and 7.8 p.p.m., of equal intensity, are attributed to the methylenic carbons C^9 and C^8 respectively, it being considered that the shift of C^8 will have more in common with the carbons of the $SiMe_2$ ring substituent.



(11)

A precedent for structure (10) is provided by that determined for $[\overline{Fe\{1—5\text{-}\eta\text{-}C_7H_8(6\text{-}CHCO_2MeC}HCO_2Me)\}(CO)_2]$ (11) by *X*-ray diffraction.[11] The migration of just one silicon from ruthenium in the formation of (10) unequivocally arises from an intramolecular process and the ring-attached $SiMe_2$ group is undoubtedly *endo* with respect to the metal. The mechanism of the reaction probably comprises an initial co-ordination of the hydrocarbon in a 1—4-η-diene mode, displacing two carbonyl groups, followed by migration of one $SiMe_2$ group with a change to the 1—5-η-dienyl mode, as shown in Scheme 1. The driving force to migration may be the evident [2-4,12] desire of the metal to achieve an η^5 mode of bonding to hydrocarbons, a desire which also prevents migration of the remaining ruthenium-bound $SiMe_2$ group. Should this second migration occur the transient species (12) would be formed with η^4-co-ordination to 16-electron ruthenium. Such double migration can, however, be induced by treatment of (10) with carbon monoxide, to give the 18-electron complex (13), as shown in Scheme 1. Thus a hexane solution of (10) at 60 °C with carbon monoxide at *ca.* 0.67 atm * pressure

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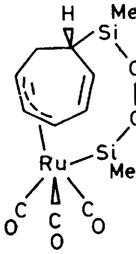
* Throughout this paper: 1 atm = 101 325 Pa; 1 mmHg $\approx 13.6 \times 9.8$ Pa.

gave in high yield a species with a carbonyl i.r. spectrum [ν(CO) at 2 059s, 1 991s, and 1 988s cm^{-1}] characteristic of a [Ru(CO)$_3$(1—4-η-diene)] complex. This spectrum can be compared with that of the known cyclohepta-1,3-diene compound [Ru(CO)$_3$(1—4-η-C$_7$H$_{10}$)] [12] [ν(CO) at 2 060m, 1 992s, and 1 988 (sh) cm^{-1}]. On bubbling carbon monoxide at atmospheric pressure through a heated heptane solution of (10) the same tricarbonyl complex was generated slowly. The product was isolated as a liquid whose mass spectrum agreed with the formulation (13), showing a molecular ion and stepwise loss of three carbonyl groups. Unfortunately the complex could not be entirely freed of hydrocarbon impurities and satisfactory analytical and n.m.r. data were not obtained.

An alternative allylic formulation (14) for the tricarbonyl compound can be discounted both on the grounds of the carbonyl i.r. spectrum and the observed irreversibility of the carbonylation. It might have been anticipated that a complex (14) would readily regenerate (10) on heating. Complex (14) is, however, the presumed intermediate in the conversion of (10) into (13). The thermal stability of (13) with respect to (10) can be correlated with the need to break a Si–C bond in forming the latter.

As a means to preparing a crystalline derivative of (13), in order to obtain analytical and n.m.r. data in support of the formulation, the C_6F_5-substituted complex (15) was prepared by treating (9) with 7-pentafluorophenylcycloheptatriene. Mass, i.r., and n.m.r. spectra (see Experimental section) of the white crystalline product were as expected for the proposed formulation (15). The related complex (16) [2] has been previously characterised by *X*-ray diffraction [13] as having *exo*-SiMe$_3$ and *endo*-C_6F_5 substituents. However, it seems certain that in the complex (15) the ring SiMe$_2$ substituent is constrained to occupy an *endo* configuration. The position of C_6F_5 is less clear, but an *exo* configuration is perhaps likely on steric grounds.



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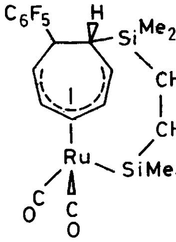

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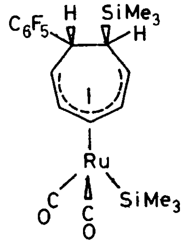
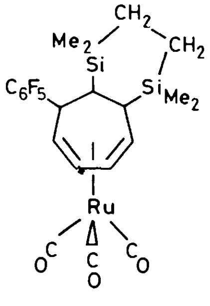


(16)

Unfortunately, although reaction of (15) with carbon monoxide afforded a tricarbonyl identified as (17) by mass and i.r. spectra (see Experimental section), it too was an oil with the purification problem encountered for (13).

Reactions of compound (10) with hydrogen and iodine, designed to cleave the Ru–Si bond and give products (18), resulted only in decomposition. Attempted hydride abstraction from (10) by [CPh$_3$][BF$_4$] likewise failed.

Reaction with Cyclo-octatetraene.—Unlike the reaction of (9) with cycloheptatriene, that with cyclo-octatetraene afforded a variety of products, formed from the migration of either one or both ends of the chelate ligand and also from the loss of the Me$_2$SiCH$_2$CH$_2$SiMe$_2$ group from ruthenium. Among the products were complexes [Ru(CO)$_3$(C$_{16}$H$_{16}$)] and [Ru$_2$(CO)$_5$(C$_{16}$H$_{16}$)] [14] of a cyclo-octatetraene dimer and the compounds [Ru$_2$(CO)$_5$-(C$_8$H$_8$)] [15,16] and [Ru$_3$(CO)$_4$(C$_8$H$_8$)$_2$] [16] of cyclo-octatetraene itself, each previously identified as being produced in the reaction of [Ru$_3$(CO)$_{12}$] with cyclo-octatetraene.



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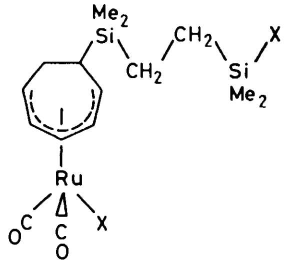
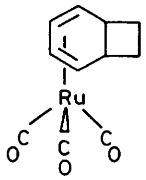
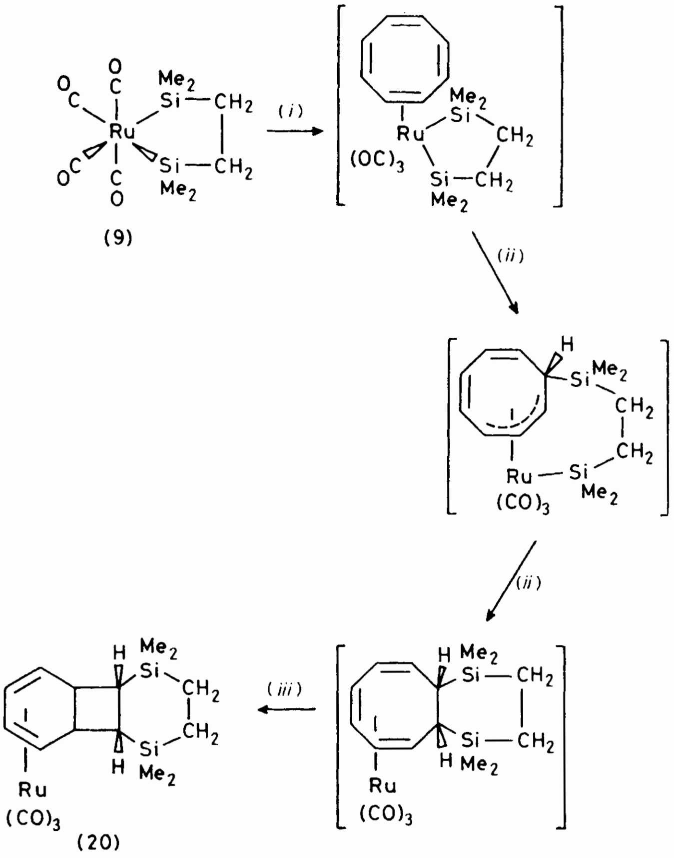


(18) X = H or I



(19)

There were, however, two other new products, resulting from migration reactions. One was a yellow liquid, obtained in high yield, and showing three carbonyl bands [ν(CO) at 2 059s, 1 994s, and 1 987s cm^{-1}] identical in frequency to those of the compound [Ru(CO)$_3$(1—4-η-C$_8$H$_{10}$)] (19).[17] This, and the mass spectrum which showed a molecular ion and ions due to loss of three carbonyl groups and to [Me$_2$SiCH$_2$CH$_2$SiMe$_2$H]$^+$, led to the formulation [Ru(C$_8$H$_8$SiMe$_2$CH$_2$CH$_2$SiMe$_2$)(CO)$_3$] (20) (Scheme 2). Despite repeated distillation (20) could not be obtained pure, but the ^{1}H n.m.r. spectrum strongly supports the proposed structure. Thus multiplets are observed at τ 3.80 (2 H) and 4.30 (2 H) corresponding to 'inner' and 'outer' protons, respectively, of a co-ordinated 1—4-η diiene, while another multiplet at τ 7.70 (2 H) is attributable to the remaining protons of the cyclohexadiene ring. The protons of the disilacyclohexane ring are observed as a multiplet centred at τ 9.11 (6 H). Four singlets at τ 9.95, 9.97, 9.99, and 10.05 of individual intensities 3 H are assigned to the methylsilyl groups, their similar high-field shifts strongly indicating that the disilicon chelate has completely migrated to the hydrocarbon. It is likely that the newly formed 1,4-disilacyclohexane ring of (20) is in a *cis,cis-endo* configuration with respect to the metal as a result of an intramolecular migration, which is envisaged to occur by the stepwise route of Scheme 2. The final ring closure of this Scheme parallels that observed in the conversion of the cyclo-octa-1,3,5-triene complex [Fe(CO)$_3$(1—4-η-C$_8$H$_{10}$)] to its bicyclo[4.2.0]octa-2,4-diene isomer.[18]



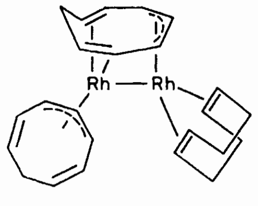
SCHEME 2 (*i*) C$_8$H$_8$, —CO; (*ii*) migration; (*iii*) ring closure

The other new product of the reaction of complex (9) with cyclo-octatetraene was isolated in low yield as yellow crystals. The mass spectrum, with ions corresponding to [Ru — *n*CO]$^+$ (*n* = 0—5), [Ru — *n*(CO + Me)]$^+$, and [Me$_2$SiCH$_2$CH$_2$SiMe$_2$H]$^+$, is consistent with the composition [Ru$_2$(Me$_2$SiCH$_2$CH$_2$SiMe$_2$)(CO)$_5$(C$_8$H$_8$)] while the i.r. spectrum shows only terminal carbonyl ligands to be present. The ^{1}H n.m.r. spectrum (see Experimental section) has signals at τ 9.56 (6 H) and 10.00 (6 H) in keeping with a migration of one silicon to the hydrocarbon and one remaining attached to ruthenium. The ring protons appear as five signals in the intensity ratio 1 : 2 : 2 : 2 : 1 and remain unchanged on cooling to —60 °C, suggesting that the evident molecular mirror plane is not generated by a fluxional process. That this is so was revealed by an *X*-ray diffraction study [9,19] of the complex, which established the structure (21) (Scheme 3).

The molecule contains a linear O–C–Ru–Ru–Si sequence with two carbonyl groups attached orthogonally to each ruthenium in an eclipsed configuration. The ruthenium atoms are symmetrically bridged by the C$_8$ ring such that one ruthenium is η^3-bonded to carbons C(4)—C(6) and the other η^2-bonded to two independent olefinic units C(2)–C(3) and C(7)–C(8). The remaining carbon [C(1)] of the ring is joined to ruthenium through a Si–C–C–Si chain derived from the original chelate.

Two related structures based on the bridging cyclo-octatrienyl (C$_8$H$_9$) ligand have been reported in recent years. That of [Rh$_2$(η^3-C$_8$H$_9$)(η^7-C$_8$H$_9$)(η^4-C$_8$H$_{12}$)] is represented as (22), and involves formally 17-electron rhodium atoms in consequence of the Rh–Rh distance of 3.036 Å, yet it is diamagnetic.[20] A somewhat different bonding mode for η^7-C$_8$H$_9$ is found in [Ru$_3$(C$_8$H$_9$)$_2$(CO)$_6$] (23), where two of the ring carbons are equidistant from each bridged ruthenium and the hydrocarbon electron density is evidently more delocalised.[21]

The determination of the molecular structure of (21) provided an insight into reactions described earlier.[1] Heating complex (4) with (1) gave yellow crystalline [Ru$_2$(C$_8$H$_8$SiMe$_3$)(SiMe$_3$)(CO)$_5$], identified as having structure (24) on the evidence that its i.r. and n.m.r. spectra were closely similar to those of (21). Heating (24) in octane liberated one molecule of carbon monoxide with opening of the C$_8$ ring, affording [Ru$_2$(C$_8$H$_8$SiMe$_3$)(SiMe$_3$)(CO)$_4$] (25).[1,19] In contrast, (21) is stable on heating in octane and does not ring-open. This difference in reactivity is readily accounted for in the linking of the two silicon atoms in (21). This prevents the considerable separation required of them on ring-opening, as seen in the structure of (25).



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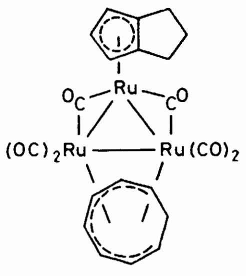

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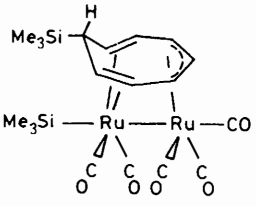

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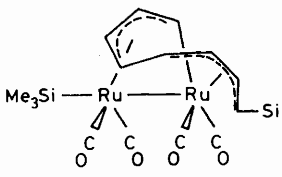
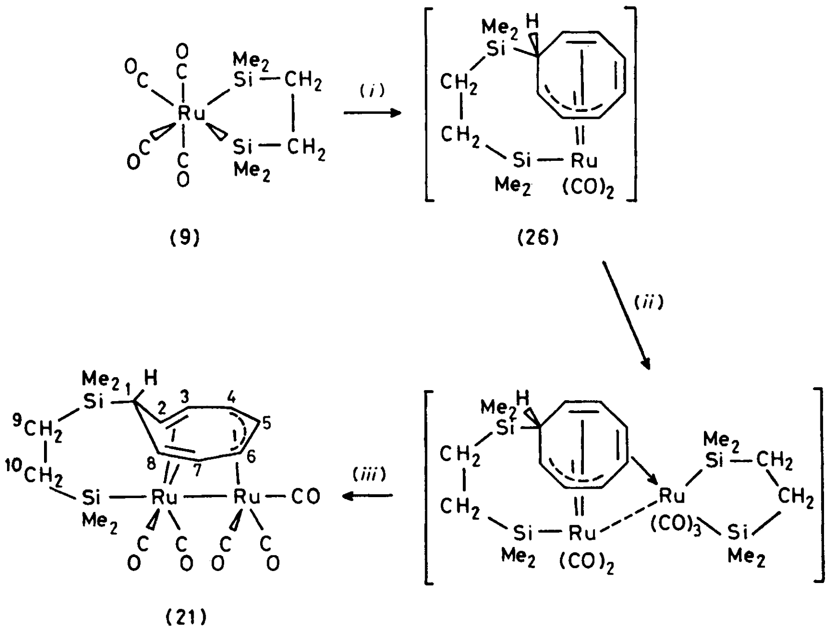


(25)

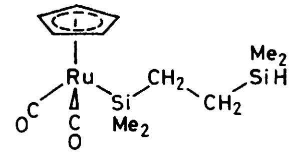
In view of the fact that (24) is formed through treating (1) with (4), we propose that (21) may arise as shown in Scheme 3. This envisages the initial formation of a complex (26) analogous to (4), which reacts with further (9), followed by reductive elimination of the Me$_2$SiCH$_2$-CH$_2$SiMe$_2$ group to afford (21).

Reactions with Cyclopentadiene.—The reaction of (1) with cyclopentadiene has been shown [12] to give the cyclopentadienyl complex [Ru(η-C$_5$H$_5$)(SiMe$_3$)(CO)$_2$], with i.r. spectroscopic evidence for the loss of an $SiMe_3$ group from ruthenium as $SiMe_3H$ being obtained. Treatment of (9) with cyclopentadiene provided an opportunity to confirm this path, since a complex (27) should arise if the reaction proceeded analogously.



Scheme 3 (*i*) C_8H_8, $-2CO$; (*ii*) complex (9), $-CO$; (*iii*) $-SiMe_2CH_2CH_2SiMe_2$

The white crystalline product obtained in good yield on treating (9) with cyclopentadiene was not, however, complex (27). The ^1H n.m.r. spectrum exhibited signals at τ 4.84 (s, 5 H), 9.24 (s, 2 H), and 9.68 (s, 6 H) typical of η-C_5H_5, methylene, and Me_2Si–Ru protons, respectively, with the ^{13}C n.m.r. spectrum showing corresponding resonances at 86.8, 18.8, and 5.3 p.p.m., plus one signal at 202.0 p.p.m. due to CO. These spectra imply a structure (28), which is supported by i.r. and analytical data. The i.r. spectrum of (28) displays two carbonyl bands at 2 013, and 1 955 cm^{-1} with distinct shoulders at 2 010 and 1 951 cm^{-1}. These frequencies are typical of an $Ru(\eta$-$C_5H_5)(CO)_2$ group attached to silicon, as revealed by the i.r. spectrum of $[Ru(\eta$-$C_5H_5)(SiMe_3)(CO)_2]$ [12] [ν(CO) 2 016 and 1 957 cm^{-1}]. Moreover, the four-band carbonyl band pattern of (28) closely resembles that of $[Fe_2\{(CH_2)_4\}(\eta$-$C_5H_5)_2(CO)_4]$, whose structure (29) has been determined by *X*-ray diffraction.[22] The presence of four bands for the latter was attributed to the existence of two conformations of the molecule in solution, arising from rotation about the Fe–CH_2R bond. A similar situation is possible with respect to the Ru–$SiMe_2R$ bond of (28). Such a conformational effect was first reported by Jetz and Graham [23] for the complex $[Fe(\eta$-$C_5H_5)(SiMeCl_2)(CO)_2]$.



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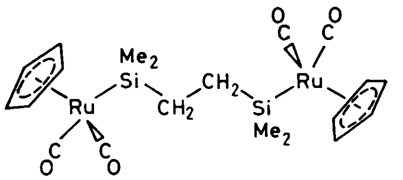

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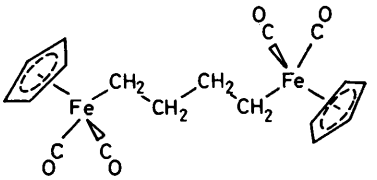

(29)

It is proposed that (9) reacts with cyclopentadiene *via* initial η^4 co-ordination of the olefin, followed by hydrogen transfer from cyclopentadiene to silicon, forming (27). Reaction of this complex with $[Ru(\eta$-$C_5H_5)H(CO)_2]$

could then yield (28). The related treatment of (1) with cyclopentadiene was observed[12] to yield [Ru(η-C_5H_5)H$(CO)_2$], lending support to this proposal.

Although the reactions of (9) described above reveal a clear propensity for migration of silicon from ruthenium to a co-ordinated hydrocarbon, comparative study of the iron analogue of (9) showed this to be unreactive in this respect. The complex [Fe($SiMe_2CH_2CH_2SiMe_2$)$(CO)_4$] was stable in the presence of cyclopentadiene, cycloheptatriene, or cyclo-octatetraene even in octane under reflux. A similar stability of [Fe$(MMe_3)_2(CO)_4$] (M = Ge or Sn) has been observed.[24]

EXPERIMENTAL

Techniques and instrumentation were as described in previous Parts of this series. Complexes [M($SiMe_2CH_2CH_2SiMe_2$)$(CO)_4$] (M = Fe or Ru) were prepared by the literature method.[8]

Reactions of [Ru($SiMe_2CH_2CH_2SiMe_2$)$(CO)_4$] (9).—*With cycloheptatriene.* Complex (9) (0.5 g, 1.4 mmol) and C_7H_8 (3 g, 32.4 mmol) were heated in heptane (200 cm^3) under reflux for 30 h. After removal of solvent at reduced pressure, the residue was chromatographed (20 cm silica column). Elution with hexane gave 0.34 g (62%) of white *crystalline* [Ru{1—5-η-C_7H_8(6-$SiMe_2CH_2CH_2SiMe_2$)}$(CO)_2$] (10), m.p. 100 °C (Found: C, 46.0; H, 6.0%; *M*, 394. $C_{15}H_{24}O_2RuSi_2$ requires C, 45.8; H, 6.1%; *M*, 394); ν(CO) at 2 018s and 1 963s cm^{-1} (hexane solution); ^{1}H n.m.r. τ 3.72 (1 H, t of d, *J* 1, 6), 4.60 (1 H, t, *J* 5), 4.79 (1 H, t, *J* 6), 6.28 (1 H, m), 6.38 (1 H, d of t, *J* 1, 9 Hz), 7.64 (2 H, m), 8.40—9.20 (5 H, m), 9.39 (3 H, s), 9.55 (3 H, s), 9.88 (3 H, s), and 10.15 (3 H, s) (CCl_3D solution); ^{13}C n.m.r. 198.1, 197.9, 103.1, 101.7, 99.1, 79.4, 74.2, 37.7, 32.3, 19.9, 8.7, 7.8, 6.4, −3.7, and −4.6 p.p.m. (downfield of $SiMe_4$) (CCl_3D solution).

With 7-Pentafluorophenylcycloheptatriene. Complex (9) (0.2 g, 0.56 mmol) and 7-$C_6F_5C_7H_7$ (0.7 g, 2.8 mmol) were heated in octane (80 cm^3) under reflux for 20 h. Treatment as above then gave 62 mg (20%) of white *crystalline* [Ru{1—5-η-C_7H_7(6-$SiMe_2CH_2CH_2SiMe_2$)(7-C_6F_5)}$(CO)_2$] (15), m.p. 161 °C (Found: C, 45.1; H, 4.4%; *M*, 560. $C_{21}H_{23}F_5O_2RuSi_2$ requires C, 45.0; H, 4.1%; *M*, 560); ν(CO) at 2 023s and 1 970s cm^{-1} (hexane solution); ^{1}H n.m.r. τ 3.54 (1 H, t, *J* 6), 4.55 (1 H, dd, *J* 4, 5), 4.69 (1 H, dd, *J* 6, 10), 5.51 (1 H, dd, *J* 1, 5), 6.42 (1 H, d of t, *J* 1, 9), 6.65 (1 H, dd, *J* 3, 10 Hz), 8.41 (2 H, m), 8.75 (3 H, m), 9.28 (3 H, s), 9.54 (3 H, s), 9.90 (3 H, s), and 10.42 (3 H, s) (CCl_3D solution).

With cyclo-octatetraene. Complex (9) (0.25 g, 0.7 mmol) and C_8H_8 (1.5 g, 14 mmol) were heated in heptane (200 cm^3) under reflux for 30 h. Chromatography as above, eluting with hexane and a gradually increasing proportion of dichloromethane (up to 1 : 3), gave in order 0.15 g (49%) of yellow *liquid* [Ru($C_8H_8SiMe_2CH_2CH_2SiMe_2$)$(CO)_3$] (20), b.p. 20 °C at 10^{-1} mmHg (Found: *M*, 434. $C_{17}H_{24}O_3RuSi_2$ requires *M*, 434); ν(CO) at 2 059s, 1 994s, and 1 987s cm^{-1} (hexane solution); ^{1}H n.m.r. τ 3.81 (2 H, m), 4.30 (2 H, m), 7.70 (2 H, m), 9.11 (6 H, m), 9.95 (3 H, s), 9.97 (3 H, s), 9.99 (3 H, s), and 10.05 (3 H, s) (CCl_3D solution); 90 mg (34%) of the known[14] [Ru$(CO)_3$($C_{16}H_{16}$)]; 6 mg (4%) of yellow *crystalline* [Ru_2($C_8H_8SiMe_2CH_2CH_2SiMe_2$)$(CO)_5$] (21), m.p. 175 °C (decomp.) (Found: C, 38.0; H, 3.9%; *M*, 591. $C_{17}H_{24}O_5Ru_2Si_2$ requires C, 38.8; H, 3.9%; *M*, 591); ν(CO) at 2 056s, 2 002, 2 000s (sh), 1 976w, and 1 955w cm^{-1} (hexane solution); ^{1}H n.m.r. τ 5.46 (1 H, t, *J* 6), 6.06 (2 H, dd, *J* 5, 7), 7.13 (2 H, dd, *J* 5, 8), 7.82 (2 H, dd, *J* 6, 8 Hz), 8.50—9.30 (5 H, m), 9.56 (6 H, s), and 10.00 (6 H, s); traces of known[14] [$Ru_2(CO)_5$($C_{16}H_{16}$)]; 12 mg (7%) of known[15,16] [$Ru_2(CO)_5$(C_8H_8)]; and traces of known[16] [$Ru_3(C_8H_8)_2(CO)_4$].

With cyclopentadiene. Complex (9) (0.5 g, 1.4 mmol) and freshly distilled C_5H_6 (1.6 g, 27 mmol) were heated in heptane (150 cm^3) under reflux for 96 h. Concentration and cooling to −30 °C of the resulting solution gave 150 mg (38%) of white *crystalline* [$(OC)_2$(η-C_5H_5)$RuSiMe_2CH_2CH_2SiMe_2Ru$(η-C_5H_5)$(CO)_2$] (28), m.p. 146 °C (Found: C, 41.3; H, 4.5. $C_{20}H_{26}O_4Ru_2Si_2$ requires C, 40.8; H, 4.4%); ν(CO) at 2 013s, 2 010s (sh), 1 955s, and 1 951s (sh) cm^{-1} (hexane solution); ^{1}H n.m.r. τ 4.84 (10 H, s), 9.24 (4 H, s), and 9.68 (12 H, s) (CCl_3D solution). The heaviest ion in the mass spectrum corresponded to [Ru(η-C_5H_5)($SiMe_2CH_2CH_2SiMe_2$)$(CO)_2$]$^+$.

Reaction of [Ru{1—5-η-C_7H_8(6-$SiMe_2CH_2CH_2SiMe_2$)}$(CO)_2$] (10) *with* CO.—A Pyrex tube (*ca.* 100 cm^3 capacity) containing complex (10) (0.16 g, 0.4 mmol), CO (500 mmHg), and hexane (20 cm^3) was heated at 60 °C for 24 h. Concentration and cooling crystallised 12 mg of [$Ru_3(CO)_{12}$]. Evaporation of the remaining solution then provided yellow *liquid* [Ru{η^4-C_7H_8($SiMe_2CH_2CH_2SiMe_2$)}$(CO)_3$] (13), b.p. 30 °C at 10^{-1} mmHg (Found: *M*, 394. $C_{17}H_{24}O_3RuSi_2$ requires *M*, 394); ν(CO) at 2 059s, 1 991s, and 1 988s cm^{-1} (hexane solution). Repeated attempts to purify the product by distillation and chromatography failed.

Reaction of [Ru{1—5-η-C_7H_7(6-$SiMe_2CH_2CH_2SiMe_2$)(7-C_6F_5)}$(CO)_2$] (15) *with* CO.—As above, a sealed tube containing (15) (0.1 g, 0.18 mmol), CO (500 mmHg), and hexane (20 cm^3) was heated at 80 °C for 3 d. Concentration and cooling crystallised 20 mg of [$Ru_3(CO)_{12}$], while evaporation of the remaining solution yielded yellow *liquid* [Ru{η^4-C_7H_7(6-$SiMe_2CH_2CH_2SiMe_2$)(7-C_6H_5)}$(CO)_3$] (17), b.p. 60 °C at 10^{-1} mmHg (Found: *M*, 588. $C_{23}H_{23}F_5O_3RuSi_2$ requires *M*, 588); ν(CO) at 2 066s and 1 997s (br) cm^{-1} (hexane solution). Repeated attempts to purify the product by distillation and chromatography failed.

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