Hydrocarbon Complexes of Ruthenium. Part II.[1] Reactions of Organo-silyl- and -germyl-(carbonyl)ruthenium Complexes with Cyclo-octatrienes

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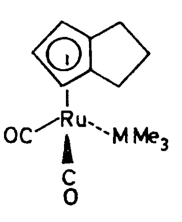
An isomeric mixture of cyclo-octa-1,3,5- and -1,3,6-trienes reacts with $[Ru(SiMe_3)_2(CO)_4]$ and with $[Ru(SiMe_3)(CO)_4]_2$ to give the non-silicon-containing complexes $[Ru_2(CO)_6(C_8H_{10})]$ and $[Ru(CO)_3(C_8H_{10})]$ as major products, as well as the tetrahydropentalenyl complex $[Ru(SiMe_3)(CO)_2(C_8H_9)]$. The germanium analogues $[Ru(GeMe_3)_2(CO)_4]$ and $[Ru(GeMe_3)(CO)_4]_2$, however, undergo Ge–Ru bond cleavage less readily in reactions with the C_8H_{10} mixture, and the tetrahydropentalenyl compound $[Ru_2(GeMe_3)(\mu\text{-}GeMe_2)_2(CO)_4(C_8H_9)]$ is the predominant product. The two complexes $[Ru_2(CO)_6(C_8H_{10})]$ and $[Ru(CO)_3(C_8H_{10})]$ are readily prepared from dodecacarbonyltriruthenium and the isomeric mixture of cyclo-octatrienes. The fluxional behaviour of $[Ru_2(CO)_6(C_8H_{10})]$ has been studied.

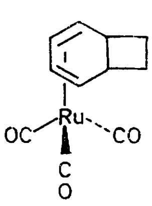
In the preceding paper, we describe reactions of cyclododeca-1,5,9-triene and cyclo-octa-1,5-diene with organo-(Group IVB)-(carbonyl)ruthenium complexes in which major skeletal rearrangements of the hydrocarbon reactants occur.[1] We have shown, moreover, that a pentalene diruthenium complex is formed by dehydrogenative ring closure of cyclo-octatetraene in the reaction of the latter with $[Ru(GeMe_3)_2(CO)_4]$.[2] In an extension of this work to other cyclic polyolefins we have studied the reactions of *cis*-$[Ru(MMe_3)_2(CO)_4]$ (I) and $[Ru(MMe_3)(CO)_4]_2$ (II) (M = Si or Ge) [3,4] with the isomeric mixture of cyclo-octa-1,3,5-triene, cyclo-octa-1,3,6-triene, and bicyclo[4.2.0]octa-2,4-diene produced [5] by reduction of cyclo-octatetraene.

Under relatively mild conditions (heptane at reflux), the C_8H_{10} mixture reacts with (I) and (II) (M = Si) to give a high proportion of ruthenium complexes which do not contain a trimethylsilyl ligand. The germanium analogues (I) and (II) (M = Ge), however, are much less susceptible to Ru–MMe_3 bond cleavage and only small amounts of complexes without such a linkage are formed. Thus with both (I) and (II) (M = Si) the three isolable products are $[Ru(SiMe_3)(CO)_2(C_8H_9)]$ (III; M = Si) (17%), $[Ru(CO)_3(C_8H_{10})]$ (IV) (15%), and $[Ru_2(CO)_6(C_8H_{10})]$ (V) (6%). The tetrahydropentalenyl complex (III) has been obtained previously [1] from the reactions of cyclododecatriene and cyclo-octadiene. The complex (IV) has been briefly mentioned as being formed by displacement of cyclo-octa-1,5-diene from $[Ru(CO)_4(C_8H_{12})]$ with cyclo-octa-1,3,5-triene.[6]

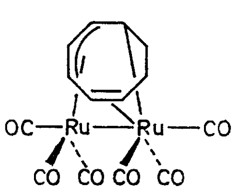
Both (IV) and (V) are more readily obtained by treating dodecacarbonyltriruthenium with the C_8H_{10} mixture in heptane at reflux. The complex (V) is not formed from (IV), but on heating (V) with the trienes in heptane, (IV) is obtained. The iron analogues of (IV) [7,8] and (V) [9] have been prepared from reactions between iron carbonyls and the cyclo-octatrienes, and the preferential coordination of the bicyclo[4.2.0]octa-2,4-diene tautomer to the $Fe(CO)_3$ system is well established.[6,10,11] Tricarbonyl(cyclo-octa-1,3,5-triene)iron is obtained under milder thermal conditions (80—100°) than those (140°) which give only the bicyclic diene complex, and has been shown [11] to undergo electrocyclic ring closure to form the latter. In the reactions studied here at 97°, only the bicyclo[4.2.0]octa-2,4-diene complex (IV) was isolated, indicating that the ring closure is facilitated by coordination of the triene to the $Ru(CO)_3$ group. The five multiplets observed in the ^1H n.m.r. spectrum of (IV) [τ 4·4 (2H), 6·5 (2H), 7·5 (2H), 8·1 (2H), and 8·8 (2H)] are in accord with the structure proposed, with assignment of the two low-field multiplets to the inner and outer diene protons respectively, and the other three multiplets to the six aliphatic protons.



(III) M = Si or Ge



(IV)



(V)

Complex (V) showed a temperature-dependent ^1H n.m.r. spectrum; we suggest that this is due to fluxional behaviour involving an oscillatory process (see Scheme) similar to that proposed for $[Ru_2(CO)_6(C_8H_8)]$ [12] and for hexacarbonyl(cyclo-octa-1,3,5-triene)di-iron.[9] At −80° (Figure) the limiting low-temperature spectrum of (V) is achieved, with two olefinic proton multiplets centred at τ 5·4 (2H) and 5·8 (3H), and a broad aliphatic proton signal between τ 8 and 9 (5H); this implies the instan-

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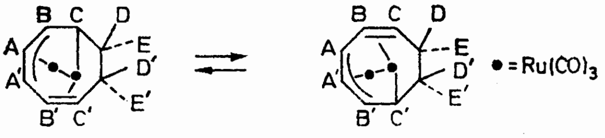
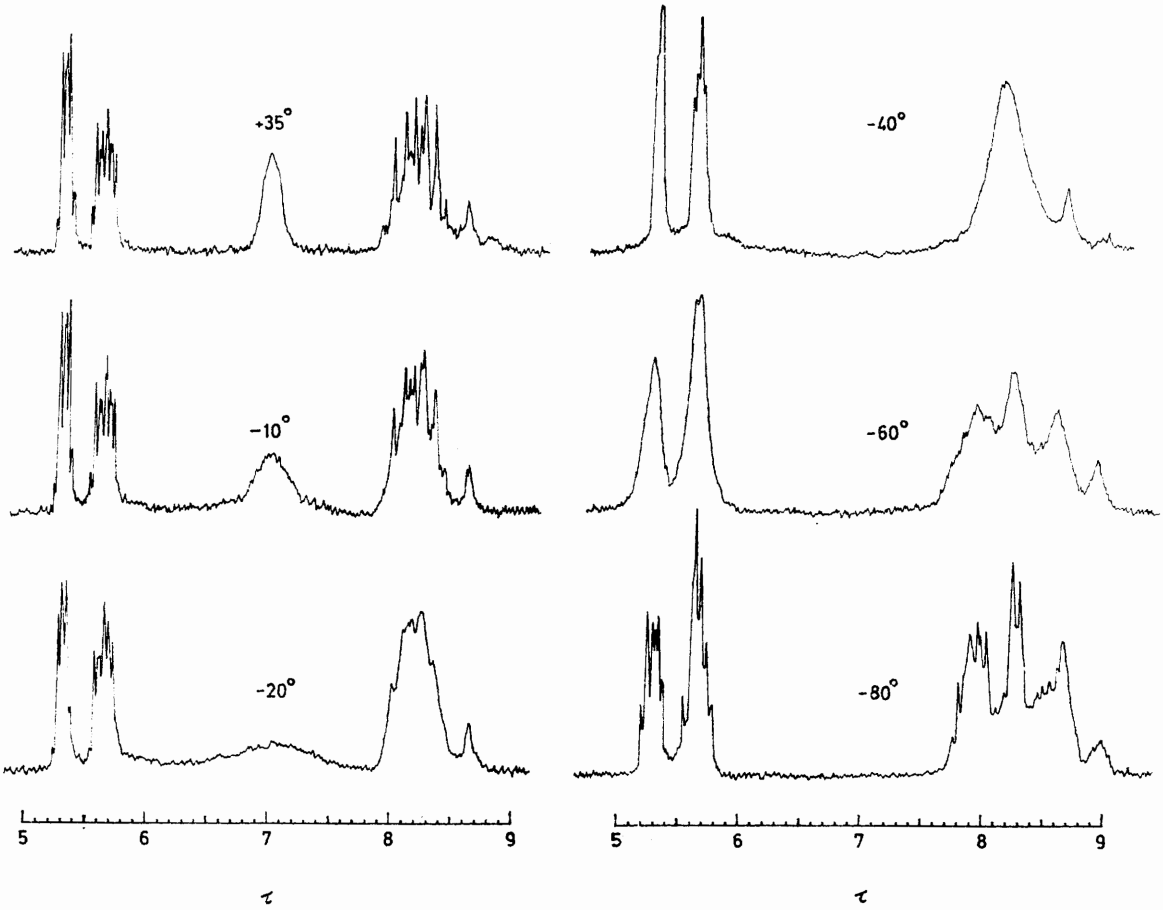
taneous structure of (V) shown. On warming, interconversion of the enantiomeric forms of (V) occurs, resulting in the time-averaged equivalence of the pairs



SCHEME

of protons A/A', B/B', C/C', D/D', and E/E'. Averaging of C and C' is reflected in the coalescence (at *ca.* −25°) of signals for an olefinic and an essentially aliphatic proton, and their eventual high temperature appearance as a single signal at τ 7·1 (2H). Other multiplets at τ 5·4 (2H), 5·8 (2H), and 8·3 (4H) at the high-temperature limit confirm the existence of a time-averaged plane of molecular symmetry.



^{1}H N.m.r. spectra of $Ru_2(CO)_6(C_8H_{10})$

Application of the approximate relationship[13] $\Delta G^{\ddagger}_{T_c} = -RT \ln (\pi h \Delta\nu/\sqrt{2}kT_c)$ to the averaging of C and C', with the temperature of coalescence $T_c = 248 \pm 5$ K and the chemical shift separation of the non-exchanging nuclei $\Delta\nu = 255 \pm 10$ Hz, gives a value for the free energy of activation of the fluxional process of 11·3 ± 0·3 kcal mol^{-1}. No comparable value for $[Fe_2(CO)_6(C_8H_{10})]$ is available, but the published spectra[9] show coalescence at about −50° of the signals due to the corresponding protons, which have roughly the same chemical shift separation. Thus it may be concluded that the fluxional process in (V) experiences a higher energy barrier than that of its iron analogue. This parallels the behaviour of the cyclo-octatetraene complexes $[M(CO)_3(C_8H_8)]$ (M = Fe, Ru, or Os).

With (I; M = Ge) the isomeric C_8H_{10} mixture reacts over 40 h in octane to give the tetrahydropentalenyl complexes (III; M = Ge) (*ca.* 10%) and $[Ru_2(GeMe_3)(\mu\text{-}GeMe_2)_2(CO)_4C_8H_9]$[1] (*ca.* 50%), in addition to the polynuclear ruthenium complexes $[Ru(GeMe_3)(\mu\text{-}GeMe_2)(CO)_3]_2$ and $[Ru(\mu\text{-}GeMe_2)(CO)_3]_3$.[4] Neither (IV) nor (V) was observed as a product of this reaction. A small amount of (V) was formed, however, by treating (II; M = Ge) with the trienes, but the major products were (III; M = Ge) and $[Ru(\mu\text{-}GeMe_2)(CO)_3]_3$.

The formation of bicyclo[3.3.0]hydrocarbon complexes from cyclo-octatrienes is unprecedented, but not surprising in view of the ability of organo-(Group IVB)-(carbonyl)ruthenium complexes to dehydrogenate and

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ring-close the more saturated cyclo-octa-1,5-diene.[1] In the case of (I) and (II) (M = Si) the preference of bicyclo[4.2.0]octa-2,4-diene for the $Ru(CO)_3$ group to a large extent predominates over the strength of the silicon–ruthenium bond and (IV) is a major product. With (I) and (II) (M = Ge), however, bicyclo[3.3.0] ring closure is induced and tetrahydropentalenyl complexes containing germanium–ruthenium bonds are formed in good yield; no complex with a bicyclo[4.2.0]octa-2,4-diene ligand is produced.

The formation of tetrahydropentalenyl complexes from cyclo-octa-1,5-diene and cyclo-octatrienes led us to investigate the reactions of cyclo-octene with (I; M = Ge) and (II; M = Si). In neither case was a product of a ring closure observed; from (I; M = Ge) only $[Ru(GeMe_3)(\mu\text{-}GeMe_2)(CO)_3]_2$ and $[Ru(\mu\text{-}GeMe_2)(CO)_3]_3$, the products of its thermal decomposition,[4] were obtained, while from (II; M = Si) the recently described [14] polynuclear ruthenium hydride $[Ru_3H_2(CO)_9(C_8H_{12})]$ was formed. Complexes of type (I) and (II) thus seem incapable of the extensive dehydrogenation necessary for formation of the tetrahydropentalenyl ligand from cyclo-octene.

EXPERIMENTAL

Instrumentation employed and general techniques were as in Part I.[1] Cyclo-octatetraene was reduced to the isomeric cyclo-octatriene mixture by an adaption of Jones' method,[15] using amalgamated zinc dust. Molecular weights were obtained by mass spectroscopy.

Reactions of the Cyclo-octatriene Mixture with Organosilicon and Organogermanium Derivatives of Ruthenium Carbonyls.—(a) *With* $[Ru(SiMe_3)_2(CO)_4]$ (I; M = Si). Compound (I; M = Si) (125 mg, 0·35 mmol) and cyclo-octatriene (150 mg, 1·41 mmol) were heated in heptane (50 ml) for 3·5 h. Removal of solvent and the excess of olefin, followed by chromatography on silica gel (elution with hexane) gave, in order of elution, yellow *liquid* $[Ru(CO)_3(C_8H_{10})]$ (IV) (15 mg, 15%) (Found: C, 45·5; H, 3·5%; *M*, 292. $C_{11}H_{10}O_3Ru$ requires C, 45·3; H, 3·4%; *M*, 292), ν_{CO}(cyclohexane) 2060s, 1994s, and 1986s cm^{-1}, purified by distillation (30° and 10^{-2} mmHg) onto a water-cooled probe, then (III; M = Si) (20 mg, 17%) identified by i.r., n.m.r., and mass spectra,[1] and finally yellow *crystalline* $[Ru_2(CO)_6(C_8H_{10})]$ (V) (5 mg, 6%), m.p. 70—71° (Found: C, 35·0; H, 2·1%; *M*, 477. $C_{14}H_{10}O_6Ru_2$ requires C, 35·3; H, 2·1%; *M*, 477), ν_{CO}(cyclohexane) 2072s, 2037s, 2006vs, 1994m, 1981m, and 1977sh cm^{-1}.

(b) *With* $[Ru(SiMe_3)(CO)_4]_2$ (II; M = Si). Complex (II; M = Si) (100 mg, 0·18 mmol) and cyclo-octatriene (110 mg, 1·03 mmol) were heated (3 h) in heptane (50 ml). Chromatography as before gave (IV) (15 mg, 15%), (III; M = Si) (20 mg, 17%), and (V) (10 mg, 12%), all identified by their i.r. and mass spectra.

(c) *With* $[Ru(GeMe_3)_2(CO)_4]$ (I; M = Ge). Complex (I; M = Ge) (265 mg, 0·59 mmol) and cyclo-octatriene (210 mg, 1·98 mmol) were heated in octane (50 ml) at reflux for 40 h. Chromatography of the involatile residue remaining after removal of solvent and olefin yielded $[Ru(GeMe_3)(\mu\text{-}GeMe_2)(CO)_3]_3$[4] (22 mg, 8%), $[Ru(\mu\text{-}GeMe_2)(CO)_3]_3$[4] (12 mg, 6%), (III; M = Ge) (20 mg, 9%), and $[Ru_2(GeMe_3)(\mu\text{-}GeMe_2)_2(CO)_4(C_8H_9)]$[1] (110 mg, 50%), each identified by i.r. and mass spectra.

(d) *With* $[Ru(GeMe_3)(CO)_4]_2$ (II; M = Ge). Compound (II; M = Ge) (120 mg, 0·24 mmol) and cyclo-octatriene (120 mg, 1·13 mmol) were heated in heptane (60 ml) for 10 h. Chromatography then gave (III; M = Ge) (20 mg, 15%), $[Ru(\mu\text{-}GeMe_2)(CO)_3]_3$ (25 mg, 24%), and (V) (5 mg, 6%), all identified by i.r. spectroscopy.

(e) *With* $Ru_3(CO)_{12}$. Cyclo-octatriene (480 mg, 2·52 mmol) and $Ru_3(CO)_{12}$ (500 mg, 0·78 mmol) were heated in heptane (80 ml) for 8 h. Chromatography as before gave (IV) (260 mg, 38%) and (V) (60 mg, 11%), identified by their i.r., n.m.r., and mass spectra.

Reactions of Cyclo-octene.—(a) *With* $[Ru(GeMe_3)_2(CO)_4]$ (I; M = Ge). A sample of (I; M = Ge) (135 mg, 0·30 mmol) and cyclo-octene (125 mg, 1·14 mmol) heated in octane (50 ml) for 55 h gave only $[Ru(GeMe_3)(\mu\text{-}GeMe_2)(CO)_3]_2$ (15 mg, 12%) and $[Ru(\mu\text{-}GeMe_2)(CO)_3]_3$ (20 mg, 23%) as identifiable (i.r.) products upon chromatography.

(b) *With* $[Ru(SiMe_3)(CO)_4]_2$ (II; M = Si). Complex (II, M = Si) (100 mg, 0·18 mmol) and cyclo-octene (100 mg; 0·91 mmol) were heated in heptane (25 ml) for 12 h, and gave $[Ru_3H_2(CO)_9(C_8H_{12})]$ (20 mg, 26%) on chromatography, identified by i.r. and mass spectra.[14]

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