Hydrocarbon Complexes of Ruthenium. Part III.[1] Reactions of Cycloheptatrienes with Ruthenium Carbonyl

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Cycloheptatriene reacts with $[Ru_3(CO)_{12}]$ in heptane to give as major product the cluster complex $[Ru_3(CO)_6(C_7H_7)(C_7H_9)]$, together with the compounds $[Ru(CO)_3(C_7H_{10})]$, $[Ru(CO)_3(C_7H_8)]$, $[Ru(CO)_2(C_7H_8)]$, and $[Ru_2(CO)_6(C_7H_8)]$. The complex $[Ru_3(CO)_6(C_7H_7)(C_7H_9)]$, which contains both a cycloheptadienyl ligand and a bridging cycloheptatrienyl ring, reacts with iodine or CX_4 (X = Cl or Br) to give the compounds $[Ru(X)(CO)_2(C_7H_9)]$ (X = Br or I) and $[Ru_2(X)(CO)_4(C_7H_7)]$ (X = Cl, Br, or I). Both $[Ru_3(CO)_6(C_7H_7)(C_7H_9)]$ and $[Ru_2(X)(CO)_4(C_7H_7)]$ contain C_7H_7 rings which are fluxional down to −100 °C. Substituted cycloheptatrienes 7R-C_7H_7 (R = Me or Ph) yield analogous complexes $[Ru_3(CO)_6(C_7H_6R)(C_7H_8R)]$ with $[Ru_3(CO)_{12}]$. These in turn give $[Ru(I)(CO)_2(C_7H_8R)]$ and $[Ru_2(I)(CO)_4(C_7H_6R)]$ with iodine. The latter are fluxional with n.m.r. spectra which are limiting at low temperatures; this, together with a knowledge of the ground-state molecular structure of $[Ru_2(I)(CO)_4(C_7H_6Ph)]$, allows an understanding of the degenerate process involved.

STUDIES of reactions of unsaturated hydrocarbons with dodecacarbonyltriruthenium appear to be establishing a substantial organic chemistry based on complexation with carbonylruthenium groups.[2] However, one of the most basic of such reactions, that of cycloheptatriene (CHT) with $Ru_3(CO)_{12}$, seemed, at the time this work was initiated, to have been overlooked. This was in spite of, or perhaps because of, the fact that cycloheptatriene derivatives of iron carbonyls $[Fe(CO)_3(C_7H_8)]$[3] and $[Fe_2(CO)_6(C_7H_8)]$[4] were well established several years ago. Differences between the chemical reactivity of iron carbonyls and $[Ru_3(CO)_{12}]$, in particular the tendency of the latter to form polynuclear ruthenium species, led us to believe that investigation of the reaction of $[Ru_3(CO)_{12}]$ with CHT would prove worthwhile.[5]

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[1] Part II, A. C. Szary, S. A. R. Knox, and F. G. A. Stone, *J.C.S. Dalton*, 1974, 662.

[2] (*a*) M. A. Bennett, ' Specialist Periodical Reports: Organometallic Chemistry,' Chemical Society, London, vols. 1—3; (*b*) F. A. Cotton, *Accounts Chem. Res.*, 1968, **1**, 257; (*c*) S. A. R. Knox and F. G. A. Stone, *ibid.*, 1974, **7**, 321.

[3] R. Burton, L. Pratt, and G. Wilkinson, *J. Chem. Soc.*, **1961**, 594; H. J. Duaben and D. J. Bertelli, *J. Amer. Chem. Soc.*, 1961, **83**, 497.

[4] G. F. Emerson, J. E. Mahler, R. Pettit, and R. Collins, *J. Amer. Chem. Soc.*, 1964, **86**, 3590.

[5] For a preliminary account see, R. Bau, J. C. Burt, S. A. R. Knox, R. M. Laine, R. P. Phillips, and F. G. A. Stone, *J.C.S. Chem. Comm.*, 1973, 726.

Treatment of dodecacarbonyltriruthenium in heptane at reflux with CHT gave as the major product (62%) a dark red crystalline trinuclear ruthenium complex $[Ru_3(CO)_6(C_7H_7)(C_7H_9)]$ (I), in addition to low yields of $[Ru(CO)_3(C_7H_8)]$ (II), $[Ru_2(CO)_6(C_7H_8)]$ (III), and a cycloheptadiene complex $[Ru(CO)_3(C_7H_{10})]$ (IV). Under u.v. irradiation $[Ru_3(CO)_{12}]$ and CHT produce only (II), in moderate (28%) yield. The ^1H n.m.r. spectrum of (I) (Table) indicated the presence of two distinctly different C_7 rings. Signals at τ 3·76 (1H, t), 4·15 (2H, m), 5·18 (2H, m), 7·50 (2H, m), and 7·95 (2H, m) are typical of a cycloheptadienyl (C_7H_9) group, while a singlet at τ 6·22 (7H) is assigned to a fluxional C_7H_7 ring. The presence of these ligands has been confirmed by a single-crystal *X*-ray diffraction study,[5,6] which shows the structure to be best represented as in (I), with a near equilateral triangle of ruthenium atoms bridged on two sides by carbonyl ligands, and on the third side by a cycloheptatrienyl ring. Of the two bridging carbonyl groups, one is markedly more asymmetric (1·85 and 2·77 Å, respectively, from each ruthenium) than the other (1·97, 2·25 Å). The latter can be assigned to the i.r. band at 1836 cm^{-1}; a weak broad absorption at 1936 cm^{-1} may be due to the partially bridging carbonyl group.

Carbonyl ruthenium complexes

Complex	Colour	M.p.(t/°C)/[b.p. (t/°C) at 10^{-2} mmHg]	Carbonyl stretching frequencies * (ν/cm^{-1})	^1H N.m.r. (τ) †
$[Ru_3(CO)_6(C_7H_7)(C_7H_9)]$ (I)	Red	155—160 dec.	2012w, 1989s, 1957s, 1936w, 1836w	3·76 (1H, t), 4·15 (2H, m), 5·18 (2H, m), 6·22 (7H, s), 7·50 (2H, m), 7·95 (2H, m)
$[Ru_3(CO)_6(C_7H_6Me)(C_7H_8Me)]$	Red	137—139 dec.	2010w, 1986s, 1953s, 1933w, 1837w	3·0—4·0m, 5·0m, 5·9m, 6·3m, 6·7m, 8·0s, 8·2s, 8·7s, 8·9d
$[Ru_3(CO)_6(C_7H_6Ph)(C_7H_8Ph)]$	Red	158 dec.	2013w, 1988s, 1956s, 1937w, 1844w	2·75m, 3·7m, 5·0m, 5·8m, 6·8m, 7·6—8·0m
$[Ru(CO)_3(C_7H_8)]$ (II)	Pale yellow	(30)	2067s, 2002s, 1991s	4·1 (1H, m), 4·55 (2H, m), 4·9 (1H, m), 6·8 (2H, m), 7·8 (2H, m)
$[Ru(CO)_3(C_7H_7Me)]$	Pale yellow	(50)	2066s, 2002s, 1990s	4·2m, 4·6m, 5·1m, 6·9m, 7·85m, 7·9s, 8·5s, 9·1d
$[Ru(CO)_3(C_7H_7Ph)]$	Pale yellow	(50)	2066s, 2003s, 1992s	2·6m, 3·0—3·5m, 6·6m, 7·2d, 7·6t of d
$[Ru(CO)_3(C_7H_{10})]$ (IV)	Pale yellow	(35)	2060s, 1992s, 1986s	4·6 (2H, m), 6·9 (2H, m), 8·15 (4H, m), 8·6 (2H, m)
$[Ru(CO)_2(C_7H_8)]$	Pale yellow		2018s, 1958s	
$[Ru_2(CO)_6(C_7H_8)]$ (III)	Yellow		2071s, 2034s, 2008vs, 1992m, 1976s	
$[Ru(Br)(CO)_2(C_7H_9)]$ (X)	Yellow	114—116	2059s, 2017s, 2012sh	3·6 (1H, t), 4·4 (2H, d of d), 5·7 (2H, m), 7·7 (2H, m), 8·3 (2H, m)
$[Ru(I)(CO)_2(C_7H_9)]$ (X)	Yellow	108—110	2053s, 2012s, 2007sh	3·7 (1H, t), 4·3 (2H, d of d), 5·6 (2H, m), 7·7 (2H, m), 8·2 (2H, m)
$[Ru(I)(CO)_2(C_7H_8Me)]$	Yellow	114—116	2054s, 2014s	3·5t, 3·6d, 5·0m, 5·9m, 7·5—8·5m, 8·7s, 8·9d
$[Ru(I)(CO)_2(C_7H_8Ph)]$	Yellow	95—97	2054s, 2013s	2·9m, 4·0—5·2m, 5·7m, 6·2m, 7·5—8·7m
$[Ru_2(Cl)(CO)_4(C_7H_7)]$ (IX)	Yellow	132—133 dec.	2043m, 2019s, 1978s, 1969m	5·9 (7H, s)
$[Ru_2(Br)(CO)_4(C_7H_7)]$ (IX)	Yellow		2042m, 2018s, 1977s, 1969m	5·9 (7H, s)
$[Ru_2(I)(CO)_4(C_7H_7)]$ (IX)	Yellow	145—148 dec.	2039m, 2016s, 1976s, 1967m	6·0 (7H, s)
$[Ru_2(I)(CO)_4(C_7H_6Me)]$ (XI)	Yellow	64—66	2041m, 2017s, 1977s, 1968m	5·4 (2H, m), 5·9 (2H, d), 6·2 (2H, m), 8·0 (3H, s)
$[Ru_2(I)(CO)_4(C_7H_6Ph)]$ (XI)	Orange	97—99	2040m, 2018s, 1975s, 1968m	2·2—2·8 (5H, m), 5·4 (2H, d), 5·5 (2H, m), 6·0 (2H, m)

* Hexane solution. † $CDCl_3$ solution.

Perhaps the most novel feature to evolve from the *X*-ray study is the C_7H_7 ring-to-metal bonding system. This can be considered, on the basis of Ru–C (ring) bond lengths, to comprise an η^3-allyl unit bonded to each of the bridged ruthenium atoms, coupled with a three centre interaction (indicated by dotted lines) involving the remaining carbon and the two ruthenium atoms, from which it is nearly equidistant (2·57 and 2·62 Å). Probably such a situation will occur, if as is apparent here, the electronic requirements (with respect to the ring) of the two metal atoms being bridged are essentially equal. One case where this criterion is satisfied has been reported previously,[4] *viz* $[Fe_2(CO)_6(C_7H_7)]^+$, which can now reasonably be reformulated with the ground-state structure (V). When the two bridged metal atoms do not have equal electronic requirements of the ring, then the cycloheptatrienyl ligand may more nearly assume a diene–allyl conformation, as has been determined by an *X*-ray diffraction study[7] on $[Ru_2(CO)_5(SiMe_3)(C_7H_6SiMe_3)]$ (VI).

The singly ' bridging ' carbon atom of (I) may be compared with the two bridging carbon atoms found by *X*-ray diffraction in several cyclo-octatetraene and pentalene complexes.[2c] Both $[Fe_2(CO)_5(C_8H_8)]$ (VII)[8] and $[Ru_2(GeMe_3)_2(CO)_4(C_8H_6)]$ (VIII),[9] for example, contain hydrocarbon ligands best represented as co-ordinated *via* an η^3-allyl unit with each metal, in association with two carbons equidistant from each metal, and involved in a multicentre interaction with them.

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[6] R. Bau and R. M. Laine, to be published.

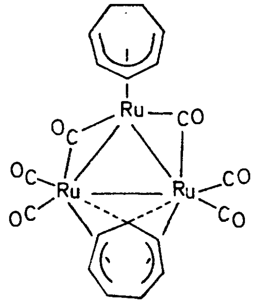
[7] A. Brookes, J. Howard, S. A. R. Knox, V. Riera, F. G. A. Stone, and P. Woodward, *J.C.S. Chem. Comm.*, 1973, 727; J. A. K. Howard and P. Woodward, *J.C.S. Dalton*, 1975, 59.

[8] E. B. Fleischer, A. L. Stone, R. B. K. Dewar, J. D. Wright, C. E. Keller, and R. Pettit, *J. Amer. Chem. Soc.*, 1966, **88**, 3158.

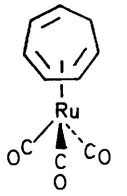
[9] A. Brookes, J. Howard, S. A. R. Knox, F. G. A. Stone, and P. Woodward, *J.C.S. Chem. Comm.*, 1973, 587.

To attempt to detail the bonding in (I) more closely than above is hazardous, for the molecule is evidently highly electron-delocalised, although there are sufficient electrons for the cluster to satisfy the Effective Atomic Number Rule overall.

The fluxional rotation of the C_7H_7 ring of (I), implicit in the single ^1H n.m.r. shift at room temperature, is maintained even at −100 °C. Changes at −100 °C in the resonances of the protons of the cycloheptadienyl ring have been attributed by Whitesides and Budnik,[10] who obtained (I) independently, to a rotation of the C_7H_9 ring relative to the Ru_3 triangle, with simultaneous interchange of the extent of asymmetry in the two bridging carbonyl ligands (see Scheme 1). This, coupled with our own studies, characterises (I) as the most spectacularly non-rigid metal cluster complex yet discovered.



(I)



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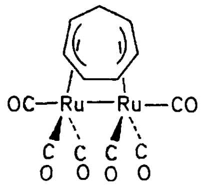

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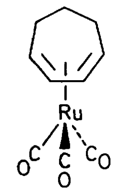
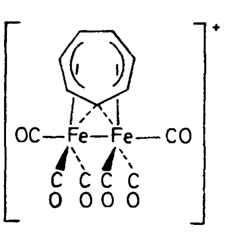
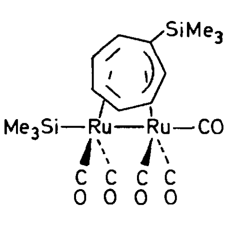


(IV)

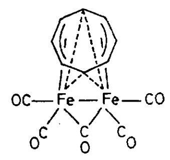


(V)

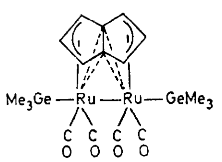


(VI)

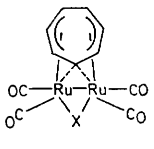
Of the minor products of the reaction of CHT with $[Ru_3(CO)_{12}]$, both (II) and (IV) have ^1H n.m.r. spectra which confirm that, as is the case for the iron analogues, the metal is co-ordinated to a 1,3-diene system. Insufficient amount of (III) was available to allow a satisfactory n.m.r. spectrum, but other data (i.r., mass spectrum, microanalysis) support the formulation of this yellow crystalline material. It is likely that the metal-to-ring bonding is as shown in (III), similar to that determined for $[Fe_2(CO)_6(C_7H_8)]$ through an X-ray diffraction study.[11]



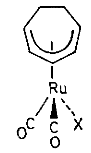
(VII)



(VIII)



(IX) X = Cl, Br, I



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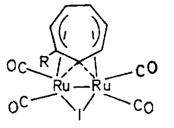
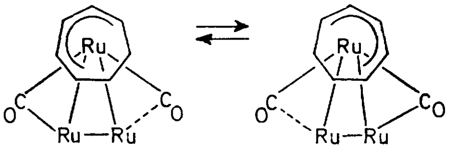


(XI) R = Me, Ph

Both (II) and (IV) have recently been briefly mentioned [12] as readily synthesised by displacement of cycloocta-1,5-diene from $[Ru(CO)_3(C_8H_{12})]$ with the appropriate olefin. We have also found that (IV) is formed in high yield from $[Ru_3(CO)_{12}]$ and cyclohepta-1,3-diene.[13] The hydrogenation process leading to the formation of (IV) from CHT and $[Ru_3(CO)_{12}]$ is also in evidence with iron carbonyls, for $[Fe(CO)_3(C_7H_{10})]$ is similarly formed from CHT and $[Fe(CO)_5]$.[3]

The CHT complex $[Fe(CO)_3(C_7H_8)]$ was initially incorrectly formulated [14-16] as a dicarbonyl $[Fe(CO)_2(C_7H_8)]$, in which all three double bonds of the olefin were envisaged as co-ordinated to the metal. From the reaction of CHT and $[Ru_3(CO)_{12}]$ we did, in fact, isolate trace amounts of a complex with a typical dicarbonyl i.r. spectrum (ν_{CO}: 2018s, 1958s cm^{-1}) whose mass spectrum showed a molecular ion and loss of two carbonyl ligands consistent with $[Ru(CO)_2(C_7H_8)]$. The trace formation of this yellow air- and solution-unstable liquid has, however, frustrated efforts to obtain n.m.r. and analytical data.



SCHEME 1

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[10] T. H. Whitesides and R. A. Budnik, *J.C.S. Chem. Comm.*, 1974, 302.

[11] F. A. Cotton, B. G. DeBoer, and T. J. Marks, *J. Amer. Chem. Soc.*, 1971, **93**, 5069.

[12] A. J. P. Domingos, B. F. G. Johnson, and J. Lewis, *J. Organometallic Chem.*, 1973, **49**, C33.

[13] S. A. R. Knox, B. A. Sosinsky, and F. G. A. Stone, to be published.

[14] T. A. Manuel and F. G. A. Stone, *J. Amer. Chem. Soc.*, 1960, **82**, 366.

[15] R. Burton, M. L. H. Green, E. W. Abel, and G. Wilkinson, *Chem. and Ind.*, 1958, 1592.

[16] R. D. Fischer, *Chem. Ber.*, 1960, **93**, 165.

In an attempt to follow the course of the reaction of CHT with $[Ru_3(CO)_{12}]$ we have investigated the inter-relations of (I)—(IV), both thermally and upon reaction with CHT. It was found that (I) was converted in low yield into (II) when refluxed with CHT in heptane, and that, conversely, (II) gave (I) in high yield when heated alone, in addition to (III). Complexes (III) and (IV) were also shown to give (I) when heated with CHT, while the dicarbonyl $[Ru(CO)_2(C_7H_8)]$ was formed from (II) with CHT. These observations suggest that the metal cluster (I) is not formed directly from $[Ru_3(CO)_{12}]$, with retention of the Ru_3 framework, but *via* initially formed (II), which is also the source of the other products.

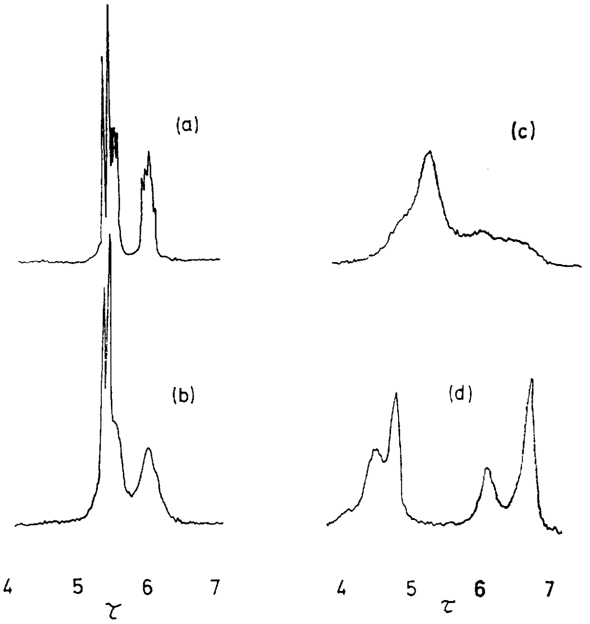
Initial separations of the mixture of products formed in the reaction of CHT with $[Ru_3(CO)_{12}]$ produced small amounts of a compound $[Ru_2(Cl)(CO)_4(C_7H_7)]$ (IX; X = Cl), shown to be formed from (I) and dichloromethane solvent during chromatography. Subsequently, we established that (I) was cleaved smoothly with iodine or carbon tetra-chloride or -bromide to give (IX; X = Cl, Br, or I) and (X; X = Br or I) on warming in hexane, or in the absence of solvent in the case of CCl_4. The compounds (X) exhibit the typical ^1H n.m.r. spectra of a co-ordinated cycloheptadienyl ligand (Table). In the i.r. region, however, they have, in addition to the expected two carbonyl stretching frequencies, a pronounced shoulder to the low-energy side of the lower absorption. Following the observation [17] of rotational isomerism in the related complexes $[Os(MMe_3)(CO)_2(C_7H_9)]$ (M = Si or Ge), it seems likely that a similar phenomenon is in evidence here, detectable by i.r. spectroscopy but not by the slower time scale of n.m.r. spectroscopy.

The crystalline cycloheptatrienyl complexes (IX) are of a new structural type. All of (IX; X = Cl, Br, or I) are fluxional molecules, exhibiting a single sharp proton n.m.r. shift between room temperature and -100 °C. In the light of both the structure of (I) and of a phenyl-substituted derivative of (IX) $[Ru_2(I)(CO)_4(C_7H_6Ph)]$ (discussed below) the symmetrically bridged ground-state structure (IX) seems likely, with the ring undergoing a series of rotational shifts so as to average the proton environments.

We extended our study to the reaction of $[Ru_3(CO)_{12}]$ with the 7-substituted methyl- and phenyl-cycloheptatrienes. The primary purpose in doing this was to obtain analogues of (I) and (IX) containing methyl or phenyl groups on the cycloheptatrienyl ring, and to study the influence of these groups on fluxional behaviour.

Reaction of $7R\text{-}C_7H_7$ (R = Me or Ph) with $[Ru_3(CO)_{12}]$ in heptane gave small amounts of the tricarbonylruthenium complexes $[Ru(CO)_3(C_7H_7R)]$, identified from i.r. and mass spectra, in addition to reasonable yields of the derivatives of (I) $[Ru_3(CO)_6(C_7H_6R)(C_7H_8R)]$. Both $[Ru_3(CO)_6(C_7H_6R)(C_7H_8R)]$ and the products of their iodine cleavage $[Ru(I)(CO)_2(C_7H_8R)]$ have complex n.m.r. spectra suggestive of the existence of isomers. This is perhaps due to positional isomerism of the R group in the cycloheptadienyl ring. Also formed upon iodine cleavage of $[Ru_3(CO)_6(C_7H_6R)(C_7H_8R)]$ were the expected analogues of (IX), *viz.* $[Ru_2(I)(CO)_4(C_7H_6R)]$. The molecular structure of $[Ru_2(I)(CO)_4(C_7H_6Ph)]$ has been established as (XI; R = Ph) by a single-crystal *X*-ray diffraction study,[18] confirming by analogy the structure assigned to the unsubstituted complexes (IX). The two ruthenium atoms (Ru–Ru = 2·86 Å) are bridged nearly symmetrically by the iodine atom (Ru–I = 2·69 and 2·71 Å), while the cycloheptatrienyl ring can, like that in (I), be approximately considered as co-ordinated *via* two η^3-allyl units and an Ru–C(H)–Ru three-centre interaction. The 'bridging' carbon is again almost equidistant (2·47 and 2·49 Å) from the two ruthenium atoms.

At 35 °C the ^1H n.m.r. spectra of the complexes (XI; R = Me or Ph) demand the existence of a mirror plane of molecular symmetry, for each has three distinct chemical shifts of equal intensity for the six cycloheptatrienyl ring protons. This is obviously inconsistent with the molecular structure determined for (XI; R = Ph) unless the mirror symmetry arises as the result of a rapid (on the n.m.r. time scale) intramolecular rearrangement which causes a pair-wise averaging of the six ring proton environments.



The ^1H n.m.r. spectrum of $[Ru_2(I)(CO)_4(C_7H_6Ph)]$ in $[^2H_6]$-acetone at (a) +35 °C, (b) -30 °C, (c) -60 °C, and (d) -100 °C

The n.m.r. spectra of (XI; R = Me or Ph) measured at various temperatures down to -100 °C confirm that a degenerate fluxional process is indeed responsible; spectra for (XI; R = Ph) are presented in the Figure. Spectra for (XI; R = Me) are very similar, differing only as a result of the different substituent effect on the ring proton shifts, and indicate that a similar fluxional process

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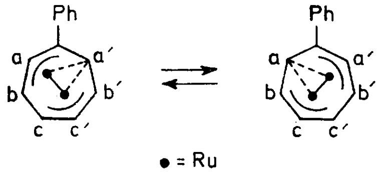
[17] S. A. R. Knox, R. P. Phillips, and F. G. A. Stone, to be published.

[18] J. A. K. Howard and P. Woodward, to be published.

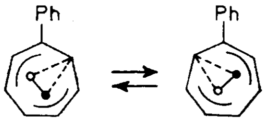
operates in each case. At −100 °C the limiting low-temperature spectrum of (XI; R = Ph) appears to be almost attained, and five resonance signals [τ 4·2 (1H), 4·5 (1H), 4·8 (1H), 6·1 (1H), and 6·7 (2H)] are observed. On warming these coalesce near −60 °C, and at +35 °C have resolved to three signals [τ 5·4 (2H, d), 5·5 (2H, d of d), and 6·0 (2H, m)].

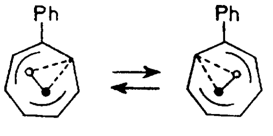
These data, taken in conjunction with the determined ground-state molecular structure, imply the degenerate oscillatory fluxional process represented in Scheme 2.



Scheme 2

This averages the pairs of protons a/a′, b/b′, and c/c′, which can be respectively assigned to the three resonance signals of the +35 °C spectrum in ascending order of field. Two possible pathways exist for the intramolecular rearrangement, which differ in that one generates equivalence of the ruthenium environments (Scheme 3) and one does not (Scheme 4). Speculation on which pathway is actually followed would be fruitless, but it is interesting to note that for the somewhat related oscillatory rearrangements of [$M_2(CO)_6(C_8H_8)$] and [$M_2(CO)_6(C_8H_{10})$] (M = Fe or Ru) complexes a similar ambiguity of pathway has been discussed.[11,19]





• = o = Ru

Scheme 3

Scheme 4

EXPERIMENTAL

Instrumentation employed and general experimental techniques were as in Part I.[20] Cycloheptatriene was obtained commercially and distilled prior to use; 7-methyl- and 7-phenyl-cycloheptatriene were prepared by the literature methods.[21,22] Heptane solvent was stirred for 24 h with concentrated sulphuric acid and dried by distillation over calcium hydride. Molecular weights were obtained by mass spectroscopy.

Reaction of Ruthenium Carbonyl with Cycloheptatriene.—(a) *Thermally.* [$Ru_3(CO)_{12}$] (0·5 g, 0·78 mmol) and CHT (1·2 g, 13·0 mmol) were heated in heptane (80 ml) at reflux for 9 h, giving a deep red solution from which solvent was removed at water pump vacuum. Chromatography (50 cm Florisil column/hexane) of the residue resulted in extensive decomposition, but gave, in order, yellow *liquid* [$Ru(CO)_3(C_7H_{10})$] (IV) (45 mg, 7%) and yellow *liquid* [$Ru(CO)_3(C_7H_8)$] (II) (55 mg, 8%), both distilled (25—50 °C/10^{-2} mmHg) and identified by i.r., n.m.r., and mass spectra (Table). Unfortunately, these species could never be completely freed of hydrocarbon impurities, and satisfactory microanalytical data were not obtained. These were followed, on elution, by traces of [$Ru(CO)_2(C_7H_8)$] (see text) and then by yellow *crystalline* [$Ru_2(CO)_6(C_7H_8)$] (III) (50 mg, 9%) (Found: C, 28·6; H, 2·4%; *M*, 463. $C_{13}H_8O_6Ru_2$ requires C, 28·7; H, 2·4%; *M*, 463).

Rapid chromatography of a similarly obtained reaction mixture on a short (*ca.* 15 cm) Florisil column, with 10% dichloromethane–hexane as eluant, gave an ill-separated mixture of (II), (III), (IV), and [$Ru(CO)_2(C_7H_8)$], followed by dark red *crystalline* [$Ru_3(CO)_6(C_7H_7)(C_7H_9)$] (I) (295 mg, 62%) (Found: C, 36·5; H, 2·5; O, 14·8; Ru, 45·9%; *M*, 657. $C_{20}H_{16}O_6Ru_3$ requires C, 36·6; H, 2·4; O, 14·7; Ru, 46·3%; *M*, 657)].

Attempted chromatography of (I) on silica gel with 10% dichloromethane–hexane caused decomposition to [$Ru_2(Cl)(CO)_4(C_7H_7)$] (IX; X = Cl).

(b) *Photochemically.* Ultraviolet irradiation (250 W mercury lamp; 60 h) of [$Ru_3(CO)_{12}$] (0·5 g, 0·78 mmol) and CHT (3 g, 32·6 mmol) in benzene (80 ml) gave (II) alone (180 mg, 28%), isolated by distillation (25 °C/10^{-2} mmHg) to a water-cooled probe.

Inter-relationship of Products from CHT–[$Ru_3(CO)_{12}$] *Reaction.*—(a) Complex (I) (50 mg, 0·08 mmol) was refluxed in heptane (30 ml) with CHT (100 mg, 1·09 mmol), and after 2 h a trace of (II) had formed. When (I) was refluxed alone in heptane there was no reaction.

(b) Complex (II) (50 mg, 0·18 mmol) was refluxed in heptane (30 ml) and after 4·5 h a trace of (III) was formed in addition to (I), which was the only product after 6 h.

(c) Reflux (4·5 h) of (II) (50 mg, 0·18 mmol) in heptane (30 ml) with CHT (100 mg, 1·09 mmol) gave approximately equal amounts of (I) and [$Ru(CO)_2(C_7H_8)$]. Chromatography on Florisil with hexane eluted [$Ru(CO)_2(C_7H_8)$) (*ca.* 20 mg, 33%).

(d) After a 2 h reflux of (III) (50 mg, 0·11 mmol) in heptane (30 ml) with CHT (100 mg, 1·09 mmol) all (III) was consumed, giving (I) in high yield. No reaction of (III) occurred when it was heated alone in heptane.

(e) Complex (IV) (40 mg, 0·14 mmol) when heated in heptane (30 ml) with CHT (100 mg, 1·09 mmol) for 1 h gave (I) alone. No reaction occurred when (IV) was heated alone in heptane.

All products described in these reactions were identified by their characteristic carbonyl i.r. spectra.

Reactions of [$Ru_3(CO)_6(C_7H_7)(C_7H_9)$] (I) *with Halogenating Reagents.*—(*a*) *With* CCl_4. When (I) (100 mg, 0·16 mmol) was warmed in CCl_4 (100 ml) for 15 min a yellow solution was formed, and removal of solvent left a yellow solid. Chromatography on silica gel with 10% dichloromethane–hexane as eluant gave (65 mg, 61%) yellow *crystals* of [$Ru_2(Cl)(CO)_4(C_7H_7)$] (IX; X = Cl) (Found: C, 30·7; H, 1·7%; *M*, 441. $C_{11}H_7ClO_4Ru$ requires C, 30·0; H, 1·6%; *M*, 441).

(*b*) *With* CBr_4. When (I) (100 mg, 0·16 mmol) was stirred in hexane (80 ml) with CBr_4 (1 g, 3 mmol) at room temperature for 7 h a yellow residue was obtained after filtration and evaporation of solvent. Chromatography on silica gel, with 10% dichloromethane–hexane, eluted 40 mg (34%) of

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$[Ru_2(Br)(CO)_4(C_7H_7)]$ (IX; X = Br) (Found: *M*, 487. $C_{11}H_7O_4BrRu_2$ requires *M*, 487). Elution with 50% dichloromethane–hexane then removed 30 mg (24%) of $[Ru(Br)(CO)_2(C_7H_9)]$ (X; X = Br) (Found: C, 34·3; H, 1·8%; *M*, 332. $C_9H_9BrO_2Ru$ requires C, 33·8; H, 1·7%; *M*, 332), a yellow solid unstable towards air when in solution.

(*c*) *With iodine*. All of (I) (100 mg, 0·16 mmol) was consumed on reflux in hexane (40 ml) with iodine (100 mg, 0·39 mmol) for 1 h. After filtration and evaporation, chromatography of the residue on silica gel gave, with 10% dichloromethane–hexane, yellow *crystalline* $[Ru_2(I)(CO)_4(C_7H_7)]$ (IX; X = I) (55 mg, 43%) (Found: C, 24·9; H, 1·4; I, 23·9%; *M*, 533. $C_{11}H_7IO_4Ru_2$ requires C, 24·9; H, 1·3; I, 23·8%; *M*, 533), and with 50% dichloromethane–hexane yellow $[Ru(I)(CO)_2(C_7H_9)]$ (X; X = I) (45 mg, 25%) (Found: C, 28·6; H, 2·4; I, 32·7%; *M*, 378. $C_9H_9IO_2Ru$ requires C, 28·7; H, 2·4; I, 33·7%; *M*, 378).

Reaction of $[Ru_3(CO)_{12}]$ *with Phenylcycloheptatriene*.—Refluxing (40 h) of $[Ru_3(CO)_{12}]$ (0·5 g, 0·78 mmol) and C_7H_7Ph (2 g, 11·9 mmol) in heptane (70 ml) followed by chromatography on Florisil gave a small amount (contaminated with C_7H_7Ph) of viscous *liquid* $[Ru(CO)_3(C_7H_7Ph)]$ (Found: *M*, 354. $C_{16}H_{12}O_3Ru$ requires *M*, 354) on elution with hexane, distilled at *ca.* 50 °C/10^{-2} mmHg, and dark red *crystalline* $[Ru_3(CO)_6(C_7H_6Ph)(C_7H_8Ph)]$ (200 mg, 32%) (Found: C, 47·5; H, 3·0%; *M*, 809. $C_{32}H_{24}O_6Ru_3$ requires C, 47·4; H, 3·1%; *M*, 809) on elution with 10% dichloromethane–hexane.

Reaction of $[Ru_3(CO)_{12}]$ *with Methylcycloheptatriene*.—After refluxing (16 h) $[Ru_3(CO)_{12}]$ (0·5 g, 0·78 mmol) and C_7H_7Me (1 g, 9·4 mmol) in heptane (50 ml), chromatography on Florisil with hexane gave a small amount of pale yellow *liquid* $[Ru(CO)_3(C_7H_7Me)]$ (Found: *M*, 292. $C_{11}H_{10}O_3Ru$ requires *M*, 292), distilled at *ca.* 50 °C (10^{-2} mmHg). Elution with 10% dichloromethane–hexane then gave (150 mg 28%) dark red $[Ru_3(CO)_6(C_7H_6Me)(C_7H_8Me)]$ (Found: C, 38·7; H, 2·9%; *M*, 685. $C_{22}H_{18}O_6Ru_3$ requires C, 38·5; H, 3·0%; *M*, 685).

Reaction of Iodine with $[Ru_3(CO)_6(C_7H_6R)(C_7H_8R)]$ (R = Me *or* Ph).—Although we have established that both $[Ru_2(I)(CO)_4(C_7H_6R)]$ and $[Ru(I)(CO)_2(C_7H_8R)]$ are formed from the iodine cleavage of $[Ru_3(CO)_6(C_7H_6R)(C_7H_8R)]$, these complexes are most conveniently prepared by treating the completed C_7H_7R–$[Ru_3(CO)_{12}]$ reaction mixtures directly with iodine, with no attempt to isolate the intermediate $[Ru_3(CO)_6(C_7H_6R)(C_7H_8R)]$ complex.

(*a*) *With* $[Ru_3(CO)_6(C_7H_6Ph)(C_7H_8Ph)]$. After heating (40 h) a mixture of $[Ru_3(CO)_{12}]$ (1 g, 1·56 mmol) and C_7H_7Ph (1·5 g, 8·9 mmol) in heptane (80 ml), the solution was allowed to cool, and to this was added iodine (0·5 g) in hexane. After the mixture had been stirred for 30 min at room temperature, solvent was removed and the residue was chromatographed on Florisil. Elution with hexane gave (300 mg, 21%) orange *crystals* of $[Ru_2(I)(CO)_4(C_7H_6Ph)]$ (Found: C, 33·6; H, 1·8%; *M*, 6·9. $C_{17}H_{11}IO_4Ru_2$ requires, C, 33·7; H, 1·9%; *M*, 609), followed, on elution with 15% dichloromethane–hexane, by yellow *crystalline* $[Ru(I)(CO)_2(C_7H_8Ph)]$ (200 mg, 9%) (Found: C, 39·7; H, 2·9%; *M*, 454. $C_{15}H_{13}IO_2Ru$ requires C, 39·8; H, 2·8%; *M*, 454).

(*b*) *With* $[Ru_3(CO)_6(C_7H_6Me)(C_7H_8Me)]$. In an exactly similar way, $[Ru_3(CO)_{12}]$ (1·0 g, 1·56 mmol) and C_7H_7Me (1·5 g, 14·2 mmol) were allowed to react (16 h), and the resultant solution was treated with iodine (0·5 g). Chromatography as above then gave *crystalline* $[Ru_2(I)(CO)_4(C_7H_6Me)]$ (300 mg, 23%) (Found: C, 26·4; H, 1·7%; *M*, 547. $C_{12}H_9IO_4Ru_2$ requires C, 26·9; H, 1·7%; *M*, 547), and $[Ru(I)(CO)_2(C_7H_8Me)]$ (100 mg, 5%) (Found: *M*, 392. $C_{10}H_{11}IO_2Ru$ requires *M*, 392), always obtained as an oily solid which did not give satisfactory analyses.

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