Reactions of Dodecacarbonyl-*triangulo*-triruthenium and Dodecacarbonyltetrahydridotetraruthenium with Mixtures of Cyclic Polyolefins

By **Adrian P. Humphries** and **Selby A. R. Knox,*** Department of Inorganic Chemistry, The University, Bristol BS8 1TS

The title complexes react with cyclopentadiene–cycloheptatriene, cyclopentadiene–cyclo-octatetraene, or cycloheptatriene–cyclo-octatetraene mixtures to yield the structurally related fluxional complexes $[Ru_3(CO)_6(\eta\text{-}C_5H_5)(\eta\text{-}C_7H_7)]$, $[Ru_3(CO)_6(\eta\text{-}C_5H_5)(\eta^7\text{-}C_8H_9)]$, $[Ru_3(CO)_6(\eta\text{-}C_7H_7)(\eta^5\text{-}C_8H_9)]$, and $[Ru_3(CO)_6(\eta^5\text{-}C_8H_9)(\eta^7\text{-}C_8H_9)]$. Each product has one hydrocarbon ligand η^5-co-ordinated to one ruthenium of a Ru_3 triangle, with the other bridging the remaining two rutheniums in an η^7 mode. Other products of these reactions include $[Ru_4(CO)_7(\eta\text{-}C_7H_7)_2]$ and $[Ru_3H(CO)_4(\eta\text{-}C_7H_7)(\eta\text{-}C_8H_8)]$ which contain fluxional bridging cycloheptatrienyl and cyclo-octatetraene rings. The $[Ru_3(CO)_6(\eta^5\text{-}L)(\eta^7\text{-}L')]$ ($L = C_5H_5$ or C_7H_7; $L' = C_7H_7$ or C_8H_9) complexes are smoothly cleaved by iodine to give $[RuI(CO)_2(\eta^5\text{-}L)]$ and $[Ru_2I(CO)_4(\eta^7\text{-}L')]$.

ALTHOUGH the reactions of metal carbonyls with cyclic polyolefins are extensively recorded in the literature,[1] no reports have yet appeared of similar reactions with mixtures of these olefins. Such reactions present, however, wide scope for the discovery of complexes of new structural types and for the study of possible coupling of the olefins. In a previous paper[2] we described the ability of carbonylruthenium complexes to promote formal Diels–Alder dimerisation of cyclo-octatetraene, while Whitesides and Budnik[3] have shown that two cyclohexa-1,3-diene molecules become coupled on reaction with $[Ru_3(CO)_{12}]$. We now describe an investigation of the reactions of the carbonylruthenium clusters $[Ru_3(CO)_{12}]$ and $[Ru_4H_4(CO)_{12}]$[4] with combinations of cyclopentadiene, cycloheptatriene, and cyclo-octatetraene.

---

[1] Particularly relevant are the following reviews: (*a*) F. A. Cotton, *Accounts Chem. Res.*, 1968, **1**, 257; (*b*) S. A. R. Knox and F. G. A. Stone, *ibid.*, 1974, **7**, 321; (*c*) G. Deganello, P. Uguagliati, L. Calligaro, P. L. Sandrini, and F. Zingales, *Inorg. Chim. Acta*, 1975, **13**, 247.

[2] A. P. Humphries and S. A. R. Knox, *J.C.S. Dalton*, 1978, preceding paper.

[3] T. H. Whitesides and R. A. Budnik, *J.C.S. Chem. Comm.*, 1973, 87.

[4] S. A. R. Knox, J. W. Koepke, M. A. Andrews, and H. D. Kaesz, *J. Amer. Chem. Soc.*, 1975, **97**, 3942.

RESULTS AND DISCUSSION

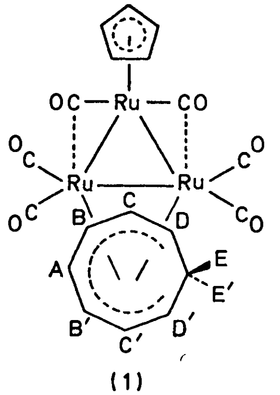
We have observed neither the coupling of the olefins nor isolated any complex in which the olefins have become joined. However, the formation of fluxional triruthenium complexes $[Ru_3(CO)_6(\eta^5\text{-L})(\eta^7\text{-L}')]$ (1), (3), and (5) containing a hydrocarbon ligand (L, L′) derived from each polyolefin of a particular mixture is general. Adjustment of the composition of each mixture of olefins to provide this 'mixed'-olefin complex in optimum yield led to the use of molar ratios of 1 : 12—15 for cyclopentadiene : cyclo-octatetraene, 1 : 5 for cyclopentadiene : cycloheptatriene, and 1 : 2—3 for cyclo-octatetraene : cycloheptatriene. Variation of these ratios directed the reaction towards that previously observed for the favoured olefin alone.

Spectroscopic and other data for the new complexes

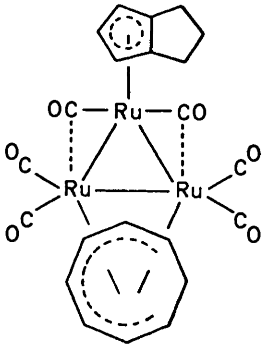
Complex	Colour	M.p. (θ_c/°C)	Carbonyl bands (cm^{-1}) [a]	^{1}H N.m.r. spectrum (τ) [b]
(1) $[Ru_3(CO)_6(\eta\text{-}C_5H_5)(\eta^7\text{-}C_8H_9)]$	Purple	195—210 (decomp.)	2 010m, 1 985vs, 1 949s, 1 931m, 1 836w,br	4.45 (5 H, s), 4.72 (1 H, t, *J* 7), 5.92 (2 H t, *J* 7), 6.94 (2 H, t of d, *J* 5,8), 7.39 (2 H, dd, *J* 7, 8), 7.53 (1 H, m), 8.74 (1 H, m)
(3) $[Ru_3(CO)_6(\eta\text{-}C_5H_5)(\eta\text{-}C_7H_7)]$	Orange	165—185 (decomp.)	2 011m, 1 987vs, 1 953s, 1 932m, 1 882vw,br	4.25 (5 H, s), 6.15 (7 H, s)
(5) $[Ru_3(CO)_6(\eta\text{-}C_7H_7)(\eta^5\text{-}C_8H_9)]$	Orange	135—145 (decomp.)	2 009m, 1 984vs, 1 950s, 1 931m, 1 877vw,br	4.48 (3 H, s, br), 6.18 (7 H, s), 4.40 (4 H, m), 7.55 (2 H, m)
(7) $[Ru_3H(CO)_4(\eta\text{-}C_7H_7)(\eta\text{-}C_8H_8)]$	Red	85—105 (decomp.)	2 014vs, 1 994s, 1 948m, 1 939m	6.08 (8 H, s), 6.88 (7 H, s), 24.92 (1 H, s)
(9) $[Ru_4(CO)_7(\eta\text{-}C_7H_7)_2]$	Black	225—240 (decomp.)	1 969s, 1 893w,br, 1 825w,br [c]	5.81 (s)
(11) $[RuI(CO)_2(\eta^5\text{-}C_8H_9)]$	Orange	50—54	2 043s, 1 997s	4.53 (1 H, t, *J* 2.5), 4.96 (2 H, d, *J* 2.5), 7.43 (6 H, m)
(12) $[Ru_2I(CO)_4(\eta^7\text{-}C_8H_9)]$	Orange	132—135	2 036s, 2 011vs, 1 971s, 1 961s	4.84 (1 H, t, *J* 6), 4.93 (1 H, t, *J* 7), 6.39 (1 H, m), 6.57 (1 H, m), 6.71 (1 H, dd, *J* 6,7), 7.09 (1 H, m), 7.17 (1 H, m), 7.22 (1 H, m), 7.78 (1 H, m)

[a] In hexane solution. [b] In $CDCl_3$ solution; *J* values in Hz. [c] In CCl_4 solution.

Treatment of $[Ru_4H_4(CO)_{12}]$ or $[Ru_3(CO)_{12}]$ in heptane under reflux with an optimised mixture of cyclopentadiene and cyclo-octatetraene gave as the major product (37 and 52% respectively) the purple crystalline complex $[Ru_3(CO)_6(\eta\text{-}C_5H_5)(\eta^7\text{-}C_8H_9)]$ (1) in addition to low yields of the bicyclo[4.2.0]octa-2,4-diene complex $[Ru(CO)_3(C_8H_{10})]$ [5] and of $[Ru_3(CO)_6(\eta^5\text{-}C_8H_9)(\eta^7\text{-}C_8H_9)]$. The latter complex, which has previously been obtained as a very minor product of the reaction of cyclo-octatetraene with $[Ru_3(CO)_{12}]$, has been shown through an *X*-ray diffraction study [6] to have a molecular structure best represented by (2). Thus a C_8H_9 ring bridges asymmetrically in an η^7 mode two ruthenium atoms of an Ru_3 triangle, while the other two edges carry 'semi-bridging' carbonyl groups. In view of the strong similarity of the i.r. spectra of (1) (Table) and of (2) [ν(CO) at 2 011m, 1 986vs, 1 951s, 1 929m, and 1 835w cm^{-1}] analogous structures are indicated. The ^{1}H n.m.r. spectrum of (1) at ambient temperature supports this in having signals attributable to an $\eta\text{-}C_5H_5$ ring [τ 4.45 (s, 5 H)] and to an $\eta^7\text{-}C_8H_9$ ring [τ 4.72 (t, 1 H), 5.92 (t, 2 H), 6.94 (t of d, 2 H), 7.39 (d of d, 2 H), 7.53 (m, 1 H), and 8.74 (m, 1 H)], the latter signals being similar to those assigned [6] to the $\eta^7\text{-}C_8H_9$ ring of (2). These data imply the existence of a mirror plane of molecular symmetry bisecting the C_8H_9 ring of (1) through the methylene carbon, *i.e.* equivalence of the pairs of protons BB′, CC′, and DD′. The solid-state molecular structure determined for (2) reveals no such equivalence of environment, so that if the structures of (1) and (2) are truly analogous then this mirror symmetry must arise as a time-averaged consequence of a rapid fluxional motion. Low-temperature ^{1}H n.m.r. studies on (1) have shown that this is indeed the case. Although the low solubility of the complex has prevented the attainment of a limiting low-temperature spectrum, at −60 °C a Fourier-transform ^{1}H n.m.r. spectrum reveals collapse almost to the point of invisibility of the signal at τ 5.92 and very substantial broadening of the signals at τ 6.94 and 7.39. The remaining signals of the C_8H_9 ring, at τ 4.72, 7.53, and 8.74, remain sharp at this temperature, indicating that the protons responsible for these signals maintain their environment throughout the process, *i.e.* that they lie on the time-averaged mirror plane. On this basis the signal at τ 4.72 must be due to proton A of (1). Double-irradiation experiments performed at ambient temperature then lead to the assignment: τ 4.72 (A), 5.92



(1)



(2)

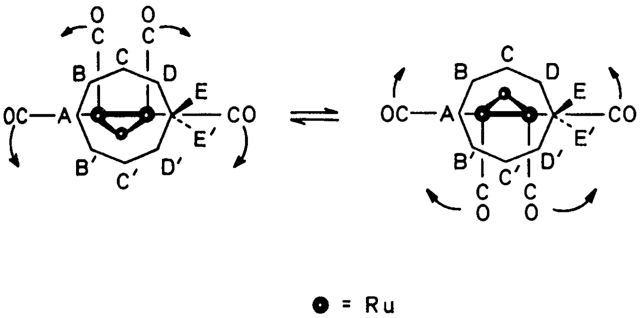
---

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

[6] R. Bau, B. C-K. Chou, S. A. R. Knox, V. Riera, and F. G. A. Stone, *J. Organometallic Chem.*, 1974, **82**, C43.

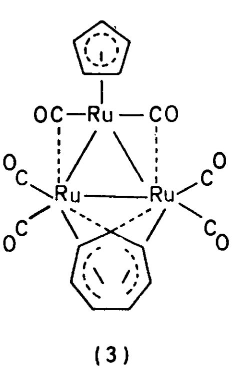
(BB'), 6.94 (DD'), 7.39 (CC'), 7.53 (E or E'), and 8.74 (E' or E) with $\overline{J(AB) + J(A'B')}$ 7, $\overline{J(BC) + J(B'C')}$ 7, and $\overline{J(CD) + J(C'D')}$ 8 Hz. The protons DD' are coupled to only one of EE' with J 5 Hz.

Similar variable-temperature n.m.r. behaviour has been recorded[6] for (2). If it is assumed, as spectroscopic data indicate is reasonable, that the instantaneous structure of (1) is closely analogous to that determined[6] for (2) then the generation of a mirror plane through the η^7-C_8H_9 ring of each species requires a substantial molecular rearrangement. A likely process can be represented in a simplified form as the oscillation:

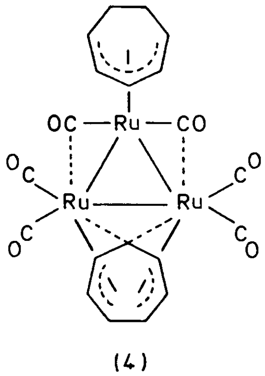


This motion comprises a rocking of the Ru_3 triangle relative to the C_8H_9 ring, accompanied by a concerted rotation of the terminal carbonyl groups on the ring-bridged ruthenium atoms. A somewhat similar process has been invoked to explain the n.m.r. spectroscopic behaviour of several pentalene complexes.[1b]

With an optimised mixture of cyclopentadiene and cycloheptatriene $[Ru_4H_4(CO)_{12}]$ gave $[\{Ru(CO)_2(\eta\text{-}C_5H_5)\}_2]$ (42%) and the cycloheptadiene complex $[Ru(CO)_3(C_7H_{10})]$ (3%), with as a minor product (4%) the orange crystalline $[Ru_3(CO)_6(\eta\text{-}C_5H_5)(\eta\text{-}C_7H_7)]$ (3), analogous to (1) and (2) and to the complex $[Ru_3(CO)_6(\eta\text{-}C_7H_7)(\eta^5\text{-}C_7H_9)]$ (4). The latter is readily obtained[7] from $[Ru_3(CO)_{12}]$ and cycloheptatriene and has been the subject of an X-ray diffraction study.[8] Only trace amounts of (3) were obtainable from $[Ru_3(CO)_{12}]$, cyclopentadiene, and cycloheptatriene. In addition to an η-C_5H_5 resonance at τ 4.25, the ^1H n.m.r. spectrum of (3), like (4), contains a temperature-invariant singlet signal [τ 6.15 (7 H)] attributable to a rapidly rotating η-C_7H_7 bridging cycloheptatrienyl ring. To this ring we assign the instantaneous η^3-allyl/' bridging ' carbon configuration established[8] for the fluxional η-C_7H_7 ring of (4).



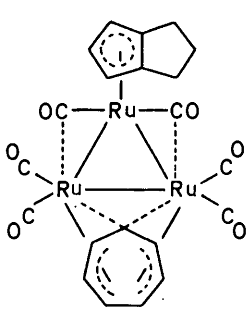
(3)



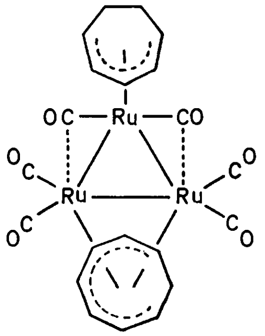
(4)

The reaction of $[Ru_4H_4(CO)_{12}]$ with a mixture of cycloheptatriene and cyclo-octatetraene was the most complex of the reactions studied, yielding about a dozen products, many in very low yield. All except four of these are also formed in the reaction of $[Ru_4H_4(CO)_{12}]$ with cyclo-octatetraene alone.[2] The others were identified as $[Ru_3(CO)_6(\eta\text{-}C_7H_7)(\eta^5\text{-}C_8H_9)]$ (5; 3%), $[Ru_3H(CO)_4(\eta\text{-}C_7H_7)(\eta\text{-}C_8H_8)]$ (7; 1%), (4; 2%), and $[Ru_4(CO)_7(\eta\text{-}C_7H_7)_2]$ (9; 2%). The reaction between this olefin mixture and $[Ru_3(CO)_{12}]$ provides complex (4) in much greater yield (27%), but is otherwise broadly similar, giving (7; 2%) and (9; 4%) but no (5).

The ^1H n.m.r. spectrum of $[Ru_3(CO)_6(\eta\text{-}C_7H_7)(\eta^5\text{-}C_8H_9)]$ is completely consistent with the formulation (5), having signals corresponding to the η^5-C_8H_9 tetrahydropentalenyl ligand [τ 4.48 (s, 3 H), 7.40 (m, 4 H), and 7.55 (m, 2 H)] and to a fluxional bridging cycloheptatrienyl ring [τ 6.18 (s, 7 H)]. Although the complex $[Ru_3(CO)_6(\eta^5\text{-}C_7H_9)(\eta^7\text{-}C_8H_9)]$ (6) was a possible alternative or co-product of this reaction, no evidence of its formation was found.



(5)



(6)

The ^1H n.m.r. spectrum of red $[Ru_3H(CO)_4(\eta\text{-}C_7H_7)(\eta\text{-}C_8H_8)]$ has singlet signals at τ 6.08 (8 H), 6.88 (7 H), and 24.92 (1 H), assigned to fluxional bridging η-C_8H_8 and η-C_7H_7 rings, and to a bridging hydride[9] ligand respectively. Only terminal carbonyl-stretching frequencies are present in the i.r. spectrum. A molecular structure related to that of the known[10] $[Ru_3(CO)_4(\eta\text{-}C_8H_8)_2]$ (8) seems probable, therefore, with an η-C_8H_8 ligand being replaced by an η-C_7H_7 ring and a bridging hydride. If both rings are considered to provide electron density equally to the ruthenium atoms to which they are co-ordinated, then 18-electron rule considerations place the bridging hydride as shown in (7a). This seems, however, intuitively less likely than a structure

---

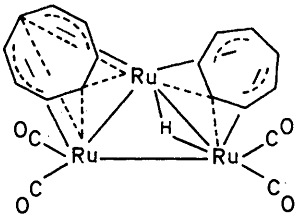
[7] J. C. Burt, S. A. R. Knox, and F. G. A. Stone, *J.C.S. Dalton*, 1975, 731.

[8] 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.

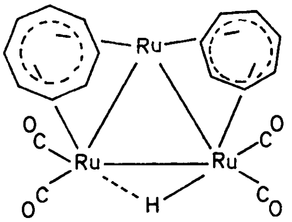
[9] H. D. Kaesz, *Chem. in Britain*, 1973, **9**, 344.

[10] M. J. Bennett, F. A. Cotton, and P. Legzdins, *J. Amer. Chem. Soc.*, 1968, **90**, 6335.

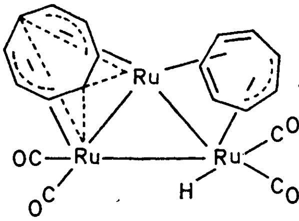
in which the hydrogen is localised over the ' open ' edge of the Ru_3 triangle. Structures (7b) and (7c) then arise. These represent extremes of the degree of asymmetric bridging which the η-C_8H_8 and η-C_7H_7 rings can accomplish, and are perhaps best viewed as canonical forms of the hydride (7d), which we propose as representing the structure. The resonance of the hydride ligand is rather low (at τ 24.92) when compared with those in, for example, $[Ru_4H_4(CO)_{12}]$ [4] (τ 27.98) and $[Ru_4H_2(CO)_{13}]$ [11] (τ 28.60), and can be attributed to some terminal hydride character {for $[RuH_2(CO)_4]$,[12] τ 17.62}, *i.e.* asymmetry in the Ru(H)Ru bridge. This most likely occurs as indicated in (7d), where (7b) is regarded as making a greater contribution to the hybrid.



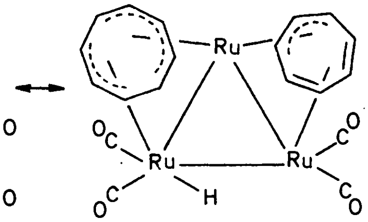
(7a)



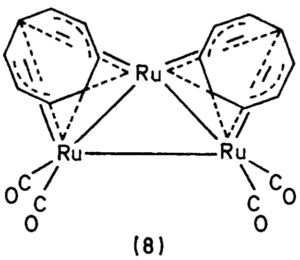
(7d)



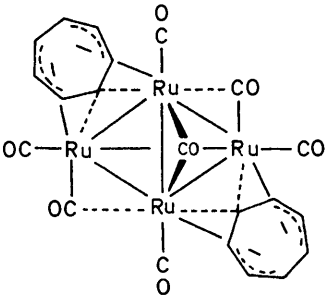
(7b)



(7c)



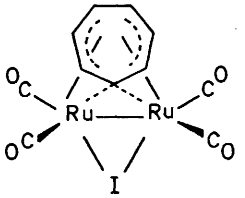
(8)



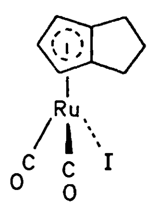
(9)

The black, fairly insoluble, tetraruthenium cluster $[Ru_4(CO)_7(\eta$-$C_7H_7)_2]$ (9) is so formulated on the basis of full elemental analyses and ^1H n.m.r. spectroscopy, which reveals only a singlet at τ 5.81, typical of fluxional bridging cycloheptatrienyl rings. The complex decomposes in the mass spectrometer, giving a spectrum identical to that of (4), while the i.r. spectrum has bands at 1 969s, 1 893w,br, and 1 825w,br cm^{-1} which are assigned to terminal, asymmetric bridging, and symmetric bridging carbonyl groups respectively. The established[13] asymmetrically bridging carbonyl groups of $[Ru_4H_2(CO)_{13}]$ appear in the i.r. spectrum at 1 881 cm^{-1}. From these data, and mindful of the 18-electron rule, the structure (9) seems a strong possibility. The existence of a tetrahedral Ru_4 skeleton is supported by the formation of (9) in 27% yield on treatment of the tetrahedrally based $[Ru_4H_4(CO)_{12}]$ with cycloheptatriene, while evidence for the $Ru_2(CO)_4(\eta$-$C_7H_7)$ unit in the molecule comes from the production of the known[7] $[Ru_2I(CO)_4(\eta$-$C_7H_7)]$ (10) on reaction of (9) with iodine.

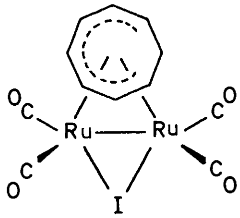
Destruction of the clusters (1), (3), and (5) also occurs on treatment with iodine in heptane under reflux. In each case the products were in accord with a smooth cleavage of $[Ru_3(CO)_6(\eta^5$-$L)(\eta^7$-$L')]$ to give $[RuI(CO)_2$-$(\eta^5$-$L)$ and $[Ru_2I(CO)_4(\eta^7$-$L')]$ in high yield. In addition to the established species $[RuI(CO)_2(\eta$-$C_5H_5)]$ and (10), new orange crystalline complexes $[RuI(CO)_2(\eta^5$-$C_8H_9)]$ and $[Ru_2I(CO)_4(\eta^7$-$C_8H_9)]$ were thus obtained. The ^1H n.m.r. spectrum (Table) of the former clearly identifies it as the tetrahydropentalenyl complex (11). The nature of the latter is of more interest. The carbonyl i.r. spectrum is very similar to that of (10), indicating a comparable structure in which the η^7-C_8H_9 ligand of the reactant complex (1) is retained, and now bridging an $Ru_2I(CO)_4$ unit. The 220-MHz ^1H n.m.r. spectrum (Table) confirms this and reveals inequivalence of all the nine protons of the hydrocarbon. The possibility of fluxional behaviour is effectively ruled out by the in-



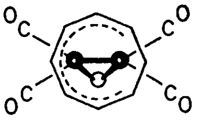
(10)



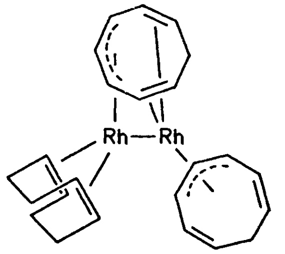
(11)



(12a)



(12b) ● = Ru
O = I



(13)

---

[11] B. F. G. Johnson, R. D. Johnston, J. Lewis, B. H. Robinson, and G. Wilkinson, *J. Chem. Soc.* (*A*), 1968, 2856.

[12] J. D. Cotton, M. I. Bruce, and F. G. A. Stone, *J. Chem. Soc.* (*A*), 1968, 2162.

[13] D. B. W. Yawney and R. J. Doedens, *Inorg. Chem.*, 1972, **11**, 838.

variance of the ^{1}H n.m.r. spectrum between −90 and 100 °C. It seems likely that the orientation of the C_8H_9 ring with respect to the bridged metal atoms is the same as that in the complexes (1) and (2)[6] from which it is derived, *i.e.* as in (12a). The inequivalence of the ring protons must therefore be due to the Ru_2I triangle not lying perpendicular to the hydrocarbon ring, as shown in (12b).

Information on the bridging η^7-C_8H_9 ligand is sparse and an *X*-ray investigation of (12) has therefore been undertaken.[14] Apart from structural determinations of (2)[6] and $[Rh_2(\eta^3\text{-}C_8H_9)(\eta^7\text{-}C_8H_9)(\eta^4\text{-}C_8H_{12})]$[15] (13) there have been only brief reports[16,17] of another complex which might contain this ligand, namely $[Fe_2(CO)_6(C_8H_9)][BF_4]$, but with no identifying data. We are reinvestigating this species and an *X*-ray diffraction study is in progress.[18] Preliminary results indicate the presence of an η^7-C_8H_9 ligand bridging an $Fe_2(CO)_6$ unit in a manner similar to that postulated in (12).

The i.r. spectra of (1)—(5) in the carbonyl-stretching region are worthy of comment. All the five complexes have a very similar four-band pattern in the region typical of terminal carbonyls, but the energy and intensity of the bridging-carbonyl-stretching bands varies markedly. Each of (1), (2), and (4) has a band at 1 835—1 840 cm^{-1}, while (3) and (5) show only weaker broad bands at 1 882 and 1 877 cm^{-1} respectively. *X*-Ray diffraction studies on (2) and (4) have characterised the asymmetric nature of the bridging carbonyl groups, and it is likely that variations in the degree of this asymmetry are reflected in the i.r. spectra of (1)—(5), with the bridges in (3) and (5) being most asymmetric, *i.e.* more nearly terminal.

Of the new complexes (1), (3), and (5), only (3) is best obtained from $[Ru_4H_4(CO)_{12}]$; otherwise the more readily available $[Ru_3(CO)_{12}]$ is a satisfactory source. However, in view of evidence[19] that $[Ru_3(CO)_{12}]$ is readily converted into $[Ru_4H_4(CO)_{12}]$ by trace amounts of moisture in hydrocarbon solvents, the possibility exists that the hydridoruthenium cluster is a reactant common to both systems.

EXPERIMENTAL

Experimental techniques and instrumentation were as described previously.[2] A Varian Associates HR220 spectrometer was used to record the ^{1}H n.m.r. spectrum of $[Ru_2I(CO)_4(\eta^7\text{-}C_8H_9)]$. Cyclopentadiene was prepared by pyrolysis of its dimer immediately prior to use, and cycloheptatriene and cyclo-octatetraene were freshly distilled.

Reactions of $[Ru_4H_4(CO)_{12}]$.[4]—(*a*) *With a cyclopentadiene–cycloheptatriene mixture.* A heptane (150 cm^3) solution of $[Ru_4H_4(CO)_{12}]$ (0.5 g, 0.67 mmol) was heated under reflux for 17 h with cyclopentadiene (0.15 g, 2.27 mmol) and cycloheptatriene (1.0 g, 10.9 mmol). Removal of solvent at reduced pressure and chromatography of the residue gave yellow, orange, and yellow bands in turn on elution with dichloromethane–hexane (1 : 1). The first band yielded *ca.* 20 mg (3%) of yellow oil, identified as tricarbonyl(η-cycloheptadiene)ruthenium by i.r. and mass spectroscopy.[20] A second band gave 20 mg (4%) of orange crystalline $[Ru_3(CO)_6(\eta\text{-}C_5H_5)(\eta\text{-}C_7H_7)]$ (3) (Found: C, 35.2; H, 2.3%; *M* 629. $C_{18}H_{12}O_6Ru_3$ requires C, 35.5; H, 1.9%; *M* 629), recrystallised from dichloromethane–hexane, while the third band contained 0.25 g (42%) of $[\{Ru(CO)_2(\eta\text{-}C_5H_5)\}_2]$, identified by i.r., mass, and ^{1}H n.m.r. spectra.

(*b*) *With cyclopentadiene–cyclo-octatetraene.* After heating $[Ru_4H_4(CO)_{12}]$ (0.5 g, 0.67 mmol), cyclopentadiene (0.12 g, 1.82 mmol), and cyclo-octatetraene (2.76 g, 26.5 mmol) in heptane (150 cm^3) under reflux for 17 h, solvent was removed and the residue subjected to chromatography. Elution with hexane gave one yellow and two red bands. These yielded, in turn, a trace amount of (η-bicyclo[4.2.0]-octa-2,4-diene)tricarbonylruthenium[5] mixed with olefin reactants, 5 mg (1%) of red crystalline $[Ru_3(CO)_6(\eta^5\text{-}C_8H_9)(\eta^7\text{-}C_8H_9)]$ (2),[6] identified by i.r., n.m.r., and mass spectroscopy, and finally 0.22 g (37%) of purple crystalline $[Ru_3(CO)_6(\eta\text{-}C_5H_5)(\eta^7\text{-}C_8H_9)]$ (1) (Found: C, 35.7; H, 2.3%; *M* 643. $C_{19}H_{14}O_6Ru_3$ requires C, 35.6; H, 2.2%; *M* 643).

(*c*) *With cycloheptatriene–cyclo-octatetraene.* The complex $[Ru_4H_4(CO)_{12}]$ (1.0 g, 1.34 mmol), cycloheptatriene (1.0 g, 10.87 mmol), and cyclo-octatetraene (0.5 g, 4.71 mmol) were heated under reflux in heptane (150 cm^3) for 17 h. Of the many products formed, most were established carbonylruthenium complexes derived from cyclo-octatetraene. However, chromatography with dichloromethane–hexane (2 : 3) separated in turn orange crystalline $[Ru_3(CO)_6(\eta\text{-}C_7H_7)(\eta^5\text{-}C_8H_9)]$ (5) (40 mg, 3%) (Found: C, 37.7; H, 2.4%; *M* 669. $C_{21}H_{16}O_6Ru_3$ requires C, 37.8; H, 2.4%; *M* 669), orange-red crystalline $[Ru_3H(CO)_4(\eta\text{-}C_7H_7)(\eta\text{-}C_8H_8)]$ (7) (5 mg, 1%) (Found: C, 37.5; H, 2.8%; *M* 613. $C_{19}H_{16}O_4Ru_3$ requires C, 37.3; H, 2.6%; *M* 613), and the known[7] red crystalline $[Ru_3(CO)_6(\eta\text{-}C_7H_7)(\eta^5\text{-}C_7H_9)]$ (4) (20 mg, 2%). Elution with dichloromethane finally removed 15 mg (1%) of black crystalline $[Ru_4(CO)_7(\eta\text{-}C_7H_7)_2]$ (9) (Found: C, 32.7; H, 1.7; O, 14.3; Ru, 51.2. $C_{21}H_{14}O_7Ru_4$ requires C, 32.2; H, 1.8; O, 14.3; Ru, 51.7%).

(*d*) *With cycloheptatriene.* After heating $[Ru_4H_4(CO)_{12}]$ (0.75 g, 1.01 mmol) and cycloheptatriene (1.0 g, 10.87 mmol) in heptane (150 cm^3) under reflux for 17 h, chromatography gave 20 mg (2%) of tricarbonyl(η-cycloheptadiene)ruthenium on elution with hexane. A benzene–hexane (1 : 1) solvent mixture then removed 0.375 g (43%) of red crystalline (4) identified by i.r., ^{1}H n.m.r., and mass spectra.[7] Final elution with benzene afforded black crystalline (9) (0.21 g, 27%), identified by i.r. and ^{1}H n.m.r. spectra.

Reactions of $[Ru_3(CO)_{12}]$.—(*a*) *With cyclopentadiene–cycloheptatriene.* Treatment of $[Ru_3(CO)_{12}]$ (0.5 g, 0.78 mmol) with cyclopentadiene (0.75 g, 11.36 mmol) and cycloheptatriene (1.0 g, 10.87 mmol) in heptane (150 cm^3) under

---

[14] W. E. Carroll and R. Bau, personal communication.

[15] J. Müller, H. O. Stühler, G. Huttner, and K. Scherzer, *Chem. Ber.*, 1976, **109**, 1211.

[16] R. B. King, *Inorg. Chem.*, 1963, **2**, 807.

[17] R. Aumann and S. Winstein, *Angew. Chem. Internat. Edn.*, 1970, **9**, 638.

[18] P. Goddard and P. Woodward, personal communication.

[19] C. R. Eady, B. F. G. Johnson, and J. Lewis, *J.C.S. Dalton*, 1977, 838.

[20] B. A. Sosinsky, S. A. R. Knox, and F. G. A. Stone, *J.C.S. Dalton*, 1975, 1633.

reflux for 17 h gave, after chromatography as above, (3) (20 mg, 4%) and $[\{Ru(CO)_2(\eta\text{-}C_5H_5)\}_2]$ (*ca.* 0.1 g, 20%).

(*b*) *With cyclopentadiene–cyclo-octatetraene.* After heating (17 h) $[Ru_3(CO)_{12}]$ (1.0 g, 1.56 mmol), cyclopentadiene (0.25 g, 3.79 mmol), and cyclo-octatetraene (5.0 g, 48.01 mmol) in heptane (150 cm^3), chromatography yielded, in turn, a trace amount of (η-bicyclo[4.2.0]octa-2,4-diene)tricarbonylruthenium, red crystalline (1) (0.52 g, 52%), and a small amount of $[\{Ru(CO)_2(\eta\text{-}C_5H_5)\}_2]$, all identified by their i.r. spectra.

(*c*) *With cycloheptatriene–cyclo-octatetraene.* The complex $[Ru_3(CO)_{12}]$ (0.75 g, 1.17 mmol), cycloheptatriene (1.0 g, 10.87 mmol), and cyclo-octatetraene (0.4 g, 3.85 mmol), after heating (17 h) in heptane, were subjected to chromatography. Elution with dichloromethane–hexane (2 : 3) afforded several known carbonylruthenium complexes of cyclo-octatetraene, and also yellow crystalline $[Ru_2(CO)_5(C_{16}H_{16})]$ [2] (15 mg, 2%), orange-red (7) (12 mg, 2%), red (4) (0.21 g, 27%), and black (9) (25 mg, 4%), each identified by their i.r. spectra.

Cleavage Reactions of Iodine.—(*a*) *With* $[Ru_3(CO)_6(\eta\text{-}C_5H_5)(\eta^7\text{-}C_8H_9)]$ (1). A solution of iodine (39.6 mg, 0.16 mmol) in heptane (40 cm^3) was slowly added to a suspension of (1) (0.1 g, 0.16 mmol) in heptane (50 cm^3) heated under reflux. After removal of the solvent the residue was chromatographed, hexane elution yielding 52 mg (70%) of yellow-orange crystalline $[Ru_2I(CO)_4(\eta^7\text{-}C_8H_9)]$ (12) (Found: C, 25.9; H, 1.7%; *M* 547. $C_{12}H_9IO_4Ru_2$ requires C, 26.4; H, 1.7%; *M* 547). Elution with dichloromethane–hexane (4 : 1) then removed unchanged (1) (11 mg) and the known orange crystalline $[RuI(CO)_2(\eta\text{-}C_5H_5)]$,[21] identified by its i.r., n.m.r., and mass spectra.

(*b*) *With* $[Ru_3(CO)_6(\eta\text{-}C_5H_5)(\eta\text{-}C_7H_7)]$ (3). As in (*a*), a heptane solution of (3) (*ca.* 10 mg) was treated with iodine in heptane slowly, until i.r. spectroscopic monitoring indicated total consumption of the complex. The known complexes $[Ru_2I(CO)_4(\eta\text{-}C_7H_7)]$ (10) [7] and $[RuI(CO)_2(\eta\text{-}C_5H_5)]$ [21] were then observed by i.r. spectroscopy to be the only products.

(*c*) *With* $[Ru_3(CO)_6(\eta\text{-}C_7H_7)(\eta^5\text{-}C_8H_9)]$ (5). Similarly, treatment of (5) (30 mg, 0.05 mmol) with iodine in heptane (50 cm^3) under reflux, followed by chromatography, yielded (10) (17 mg, 71%) on elution with dichloromethane–hexane (2 : 3). Further elution with dichloromethane–hexane (4 : 1) then afforded (14 mg, 80%) orange crystalline $[RuI(CO)_2(\eta^5\text{-}C_8H_9)]$ (11) (Found: C, 31.1; H, 2.5%; *M* 390. $C_{10}H_9IO_2Ru$ requires C, 30.9; H, 2.3%; *M* 390).

(*d*) *With* $[Ru_4(CO)_7(\eta\text{-}C_7H_7)_2]$ (9). To a dichloromethane (50 cm^3) solution of (9) (50 mg, 0.06 mmol) at room temperature, a solution of iodine in the same solvent was added dropwise until i.r. spectroscopy revealed the absence of the initial complex. Chromatography with dichloromethane–hexane (1 : 4) as eluant then gave a few mg of yellow (10), identified by i.r. and ^{1}H n.m.r. spectroscopy.[7]

We are grateful to the S.R.C. for the award of a Research Studentship, and to Johnson, Matthey and Co. Ltd. for a loan of ruthenium trichloride.

[8/068 *Received*, 16*th January*, 1978]

---

[21] A. Davison, J. A. McCleverty, and G. Wilkinson, *J. Chem. Soc.*, 1963, 1133.