Formal Diels–Alder Dimerisation of Cyclo-octatetraene induced by Carbonylruthenium Complexes

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Heating cyclo-octatetraene (cot) in heptane with $[Ru_4H_4(CO)_{12}]$ yields a previously unknown dimer of cot formally due to Diels–Alder self-addition, and derivatives $[Ru(CO)_3(C_{16}H_{16})]$ and $[Ru_2(CO)_5(C_{16}H_{16})]$. These complexes are also formed on reaction of $[Ru_3(CO)_{12}]$ with cot, but no free dimer is produced. Evidence for the intermediacy of $[Ru(CO)_3(\eta^4\text{-}C_8H_8)]$ in these reactions is provided by its yielding both cot dimer complexes on treatment with cot. A complex $[Fe(CO)_3(C_{16}H_{16})]$ of a known cot dimer is obtained when $[Fe(CO)_3(\eta^4\text{-}C_8H_8)]$ is heated with cot. Reaction of the new dimer with $[Fe_2(CO)_9]$ provides its tricarbonyliron complex, while $[Ru_3(CO)_{12}]$ yields $[Ru(CO)_3(C_{16}H_{16})]$ and also $[Ru_3H_2(CO)_9(C_{16}H_{14})]$. The complex $[Ru_2(CO)_5(C_{16}H_{16})]$, which undergoes a unique fluxional process, is readily carbonylated to give $[Ru_2(CO)_6(C_{16}H_{16})]$, a fluxional cyclo-octatriene-based species. Mechanisms of the cot dimerisations are discussed and a stepwise metal template path is favoured.

THE concept of hydridometal cluster complexes providing a link between soluble molecular complexes (homogeneous catalysis) and interstitial hydrogen or hydrogen chemisorbed on a metal surface (heterogeneous catalysis) has been a strong motivation in their study.[1] This study was retarded for many years, however, by their generally low accessibility. The discovery [2] of convenient syntheses of complexes $[M_4H_4(CO)_{12}]$ (M = Ru or Os) and $[Os_3H_2(CO)_{10}]$ therefore attracted considerable interest, particularly in regard to their reactivity towards unsaturated hydrocarbons. Previously, only $[Mn_3H_3$-

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

[2] S. A. R. Knox, J. W. Koepke, M. A. Andrews, and H. D. Kaesz, *J. Amer. Chem. Soc.*, 1975, **47**, 3942.

$(CO)_{12}]$ had received such attention,[3] but now reactions of $[Os_3H_2(CO)_{10}]$,[4-12] $[Os_4H_4(CO)_{12}]$,[13] and $[Ru_4H_4(CO)_{12}]$ [14-19] with a variety of olefins and acetylenes have been reported. In this paper we describe the formal Diels–Alder dimerisation of cyclo-octatetraene, effected by $[Ru_4H_4(CO)_{12}]$ and other carbonylruthenium complexes; aspects of this work have appeared as preliminary communications.[20]

RESULTS AND DISCUSSION

The hydridometal cluster $[Ru_4H_4(CO)_{12}]$ was consumed over *ca.* 1 d when treated with an excess of freshly distilled cyclo-octatetraene (cot) in heptane at reflux. A mixture of products was obtained which were conveniently separated by chromatography on silica gel or alumina. Several of these have been previously characterised as products of the reaction of $[Ru_3(CO)_{12}]$ with cot; namely, the pentalene complex $[Ru_3(CO)_8(C_8H_6)]$,[21] the cyclo-octatrienyl complex $[Ru_3(CO)_6(\eta^5\text{-}C_8H_9)(\eta^7\text{-}C_8H_9)]$,[22] and the cyclo-octatetraene complex $[Ru_2(CO)_5(C_8H_8)]$.[23] Also formed in low yield were two complexes of cyclo-octatriene, $[Ru(CO)_3(C_8H_{10})]$ and $[Ru_2(CO)_6(C_8H_{10})]$, each best obtained by reaction of $[Ru_3(CO)_{12}]$ with the olefin.[24] There are, in addition, three products which have not previously been mentioned as formed in the reaction of $[Ru_3(CO)_{12}]$ with cot (in fact, two of these can be so formed; see below). Mass, i.r., and n.m.r. (^1H and ^{13}C) spectra (Table) and elemental analyses indicate that these products are a new dimer of cot, $C_{16}H_{16}$ (1a), and two carbonylruthenium complexes thereof, $[Ru(CO)_3(C_{16}H_{16})]$ and $[Ru_2(CO)_5(C_{16}H_{16})]$.

The new hydrocarbon was obtained from chromatography as a mixture with $[Ru(CO)_3(C_{16}H_{16})]$ present as a minor component, from which it could not be separated by either crystallisation or sublimation. It was isolated in a pure state by treating the mixture with trimethylamine oxide in benzene at reflux, a procedure [25] which rapidly and efficiently removed the co-ordinated $Ru(CO)_3$ group, providing *ca.* 300 mg of $C_{16}H_{16}$ per gram of $[Ru_4H_4(CO)_{12}]$ employed.

The mass spectrum of the colourless, crystalline, slightly air- and light-sensitive hydrocarbon showed a molecular ion in accord with the formulation $C_{16}H_{16}$, while its nature as a dimer of cot was indicated strongly by the presence of an intense ion assignable to $[C_8H_8]^+$. The ^1H n.m.r. spectrum (Table) showed the presence of 10 olefinic and six aliphatic protons per molecule, a feature supported by the ^{13}C n.m.r. spectrum [Figure 1(b)], which revealed three *sp*^{3} (at 33.2, 34.1, and 52.1

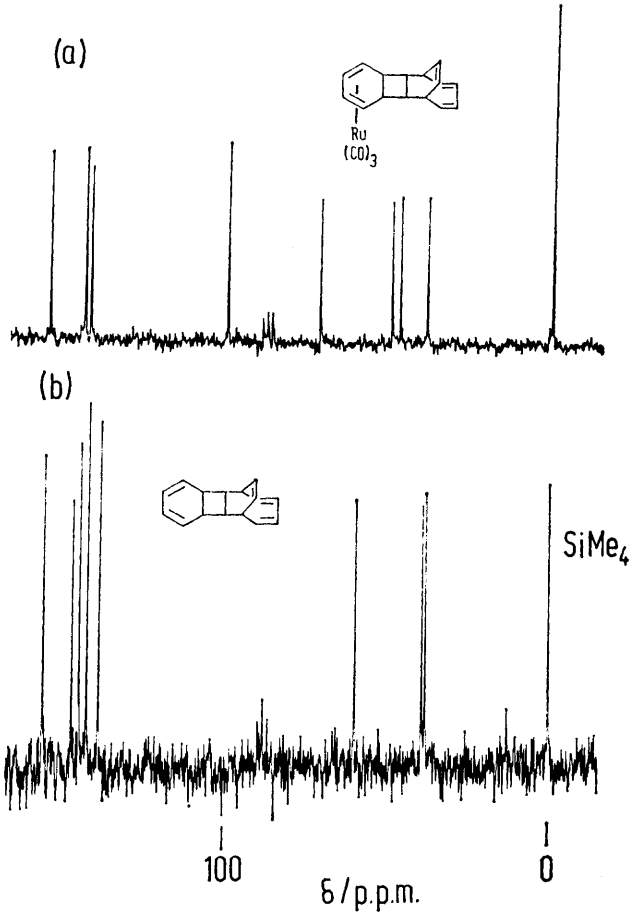

FIGURE 1 $^{13}C\text{-}\{^1H\}$ N.m.r. spectra of (a) $[Ru(CO)_3(C_{16}H_{16})]$ (6a) and (b) $C_{16}H_{16}$ (1a) in $CDCl_3$ solutions

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[3] R. B. King and M. N. Ackermann, *Inorg. Chem.*, 1974, **13**, 637.

[4] A. J. Deeming, S. Hasso, and M. Underhill, *J.C.S. Dalton*, 1975, 1614.

[5] J. B. Keister and J. R. Shapley, *J. Organometallic Chem.*, 1975, **85**, C29.

[6] J. B. Keister and J. R. Shapley, *J. Amer. Chem. Soc.*, 1976, **98**, 1056.

[7] W. G. Jackson, B. F. G. Johnson, J. W. Kelland, J. Lewis, and K. Schorpp, *J. Organometallic Chem.*, 1975, **87**, C27.

[8] E. G. Bryan, B. F. G. Johnson, J. W. Kelland, J. Lewis, and M. McPartlin, *J.C.S. Chem. Comm.*, 1976, 254.

[9] E. G. Bryan, B. F. G. Johnson, and J. Lewis, *J. Organometallic Chem.*, 1976, **122**, 249.

[10] M. Tachikawa, J. R. Shapley, R. C. Haltiwanger, and C. G. Pierpoint, *J. Amer. Chem. Soc.*, 1976, **98**, 4651.

[11] M. Tachikawa and J. R. Shapley, *J. Organometallic Chem.*, 1977, **124**, C19.

[12] E. G. Bryan, B. F. G. Johnson, and J. Lewis, *J.C.S. Dalton*, 1977, 1328.

[13] B. F. G. Johnson, J. W. Kelland, J. Lewis, and S. K. Rehani, *J. Organometallic Chem.*, 1976, **113**, C42.

[14] M. Valle, D. Osella, and G. A. Vaglio, *Inorg. Chim. Acta*, 1976, **20**, 213.

[15] P. Frediani, M. Bianchi, and F. Piacenti, *Chem. Ind. (Milan)*, 1971, **53**, 80.

[16] A. J. Canty, B. F. G. Johnson, J. Lewis, and J. R. Norton, *J.C.S. Chem. Comm.*, 1972, 1331.

[17] G. M. Sheldrick and J. P. Yesinowski, *J.C.S. Dalton*, 1975, 873.

[18] A. J. Canty, A. J. P. Domingos, B. F. G. Johnson, and J. Lewis, *J.C.S. Dalton*, 1973, 2056.

[19] A. P. Humphries and S. A. R. Knox, *J.C.S. Dalton*, 1975, 1710.

[20] R. Goddard, A. P. Humphries, S. A. R. Knox, and P. Woodward, *J.C.S. Chem. Comm.*, 1975, 507, 508.

[21] J. A. K. Howard, S. A. R. Knox, V. Riera, F. G. A. Stone, and P. Woodward, *J.C.S. Chem. Comm.*, 1974, 452.

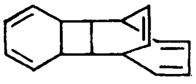
[22] R. Bau, B. C-K. Chou, S. A. R. Knox, V. Riera, and F. G. A. Stone, *J. Organometallic Chem.*, 1974, **82**, C43.

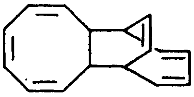
[23] F. A. Cotton, A. Davison, T. J. Marks, and A. Musco, *J. Amer. Chem. Soc.*, 1969, **91**, 6598.

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

[25] Y. Shvo and E. Hazum, *J.C.S. Chem. Comm.*, 1974, 336.

p.p.m.) and five sp^2 (at 121.0, 124.2, 126.3, 128.1, and 135.8 p.p.m. downfield of $SiMe_4$) carbon environments. There is evidently a mirror plane of molecule symmetry. These data are incompatible with any of the four known thermally produced dimers of cot (2)—(5), and point to a structure (1a). The presence of a bicyclo[4.2.0]octadiene unit is confirmed by the u.v. spectrum which exhibits a characteristic maximum at 263 nm (ε 4 600 dm^3 mol^{-1} cm^{-1}) with a shoulder at 212 nm (ε 3 800 dm^3 mol^{-1} cm^{-1}); comparable maxima are observed for (3) (282 nm, ε 2 300 dm^3 mol^{-1} cm^{-1})[26] and for bicyclo[4.2.0]octadiene itself (274 nm, ε 3 340 dm^3 mol^{-1} cm^{-1}).[27]


(1a)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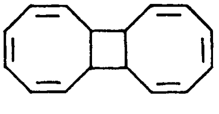
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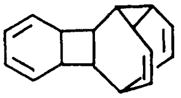
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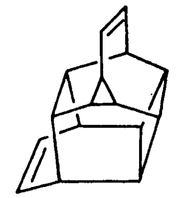
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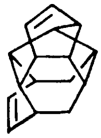
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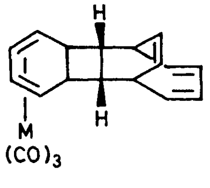
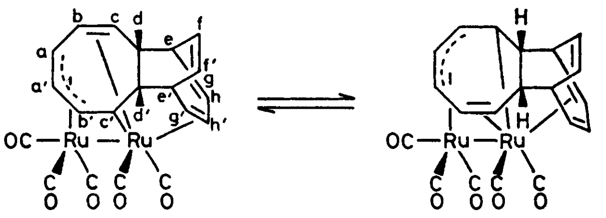


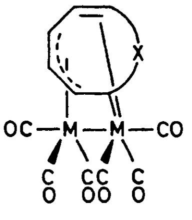
(6a) M = Ru
(6b) M = Fe

We have been unable to obtain crystals of the hydrocarbon suitable for an *X*-ray diffraction study. However, the ^{1}H (Table) and ^{13}C [Figure 1(a)] n.m.r. spectra of pale yellow crystalline [$Ru(CO)_3(C_{16}H_{16})$] {obtained pure from the reaction of cot with [$Ru_3(CO)_{12}$] (see below)} clearly suggested its identity as a complex of the new dimer and that the dimer, whatever its structure, had not suffered any gross structural change on complexation. Thus the ^{13}C n.m.r. spectrum of the complex differs from that of the dimer only in the shift to high field of two pairs of formerly olefinic carbons which have become complexed (Figure 1). Moreover, treatment of pure [$Ru(CO)_3(C_{16}H_{16})$] with NMe_3O provided the free hydrocarbon almost quantitatively. It was therefore apparent that the elucidation of the molecular structure of [$Ru(CO)_3(C_{16}H_{16})$] would, by implication, establish that of the free hydrocarbon. An *X*-ray diffraction study[20,28] was undertaken for this purpose, determining the structure (6a) for [$Ru(CO)_3(C_{16}H_{16})$] and thereby confirming the structure (1a) for the new dimer.

The complex of formulation [$Ru_2(CO)_5(C_{16}H_{16})$], isolated as bright yellow crystals, was evidently fluxional in view of its temperature-dependent ^{1}H n.m.r. spectrum (Figure 2). However, the limiting low-temperature spectrum, apart from showing the inequivalence of the 16 protons of the hydrocarbon, was not structurally revealing and an *X*-ray diffraction study was initiated. This established[20,28] the structure (7); *i.e.* [$Ru_2(CO)_5(C_{16}H_{16})$] is a complex in which the new dimer of cot adopts the configuration (1b), the cyclo-octa-1,3,5-triene valence tautomer of (1a). Complex (7) is closely related to a number of other species, of which [$Ru_2(CO)_6(C_8H_8)$][29] (8a) and [$Fe_2(CO)_6(C_8H_{10})$][30] (8b) are exemplary, each having $\eta^1 : \eta^2 : \eta^3$ co-ordination of a C_8 ring to



(7a) (7b)



(8a) M = Ru, X = CH=CH
(8b) M = Fe, X = CH_2CH_2

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[26] G. Schröder, *Angew. Chem. Internat. Edn.*, 1963, **2**, 481.

[27] G. Schröder, *Chem. Ber.*, 1964, **97**, 3131.

[28] R. Goddard and P. Woodward, unpublished work.

[29] F. A. Cotton and W. T. Edwards, *J. Amer. Chem. Soc.*, 1968, **90**, 5412.

[30] F. A. Cotton and W. T. Edwards, *J. Amer. Chem. Soc.*, 1969, **91**, 843.

an $M_2(CO)_6$ unit. For (7), additionally, one ruthenium exhibits an η^2 interaction with an olefinic bond of a 'substituent' C_8 ring.

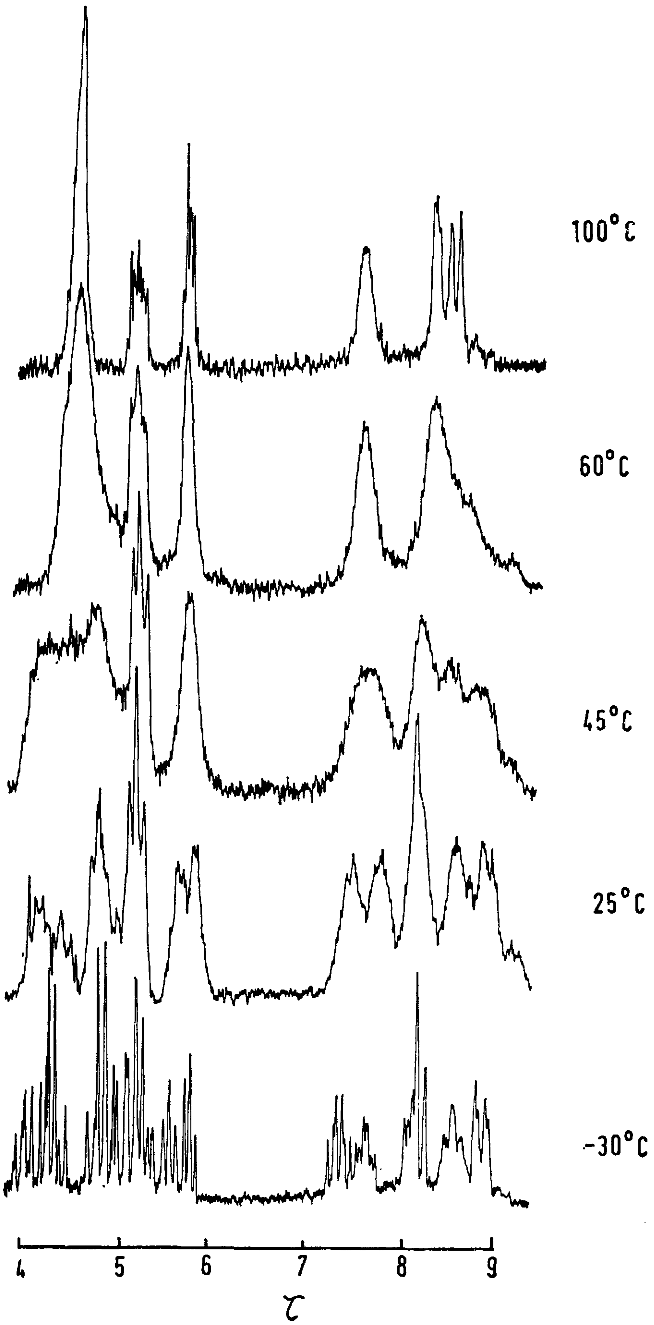

FIGURE 2 Hydrogen-1 n.m.r. spectrum of $[Ru_2(CO)_5(C_{16}H_{16})]$ (7) in chlorobenzene solution at various temperatures

The crystallographic asymmetric unit of (7) comprises two distinct molecules which do not differ significantly from one another. However, since the space group is centrosymmetric each molecule is one of an enantiomorphous pair, which are related as (7a) and (7b). It is interesting in this light that the fluxional behaviour of the complex in solution (Figure 2) is consistent with a (7a) $\rightleftharpoons$ (7b) interconversion. Although the limiting low-temperature spectrum shows the complexity to be expected of a molecule having instantaneous structure (7a) or (7b), at the fast-exchange limit the spectrum implies the generation of a time-averaged mirror plane of molecular symmetry. In this spectrum (100 °C) the three multiplets at lowest field can be confidently attributed to the five pairs of protons aa', bb', ff', gg', and hh', although without individual assignment. The two highest-field multiplets can also be attributed clearly to the pairs dd' and ee'. The multiplet at an intermediate shift of τ 7.60 (2 H) is proposed to arise from the averaging of the c (olefinic) and c' (aliphatic) protons, which provide the low-temperature signals at τ 7.46 and 7.74 respectively.

The fluxional process suggested to occur for the $\eta^1:\eta^2:\eta^3$-bonded C_8 ring of (7) is identical to that previously invoked to account for the temperature-dependent n.m.r. spectra of $[Ru_2(CO)_6(C_8H_8)]$ [29] and $[Fe_2(CO)_6(C_8H_{10})]$.[30-32] The simultaneous interchange of η^2 bonding within the other ring provides, however, a rare example of a fluxional 1,3-shift rearrangement. Such shifts are otherwise only established for the complexes $[Fe(CO)_3(\eta^4\text{-}C_7H_8)]$,[33] $[Cr(CO)_3(\eta^6\text{-}C_8H_8)]$,[34] and a variety of cycloheptadienyl and cyclo-octadienyl complexes of palladium.[35]

Application of relation [36] (1) to the averaging of

$$\Delta G^\ddagger = -RT_c\ln(\pi h\Delta\nu/2^{\frac{1}{2}}kT_c) \qquad (1)$$

protons c and c' provides an approximate value for the free energy of activation of the fluxional process of 16.0 ± 0.3 kcal mol^{-1} (T_c 318 ± 5 K, $\Delta\nu$ 28 ± 1 Hz),* which is markedly higher than the value of 11.3 ± 0.3 kcal mol^{-1} reported for $[Ru_2(CO)_6(C_8H_{10})]$ [24] and in accord with the required additional 1,3 shift of the η^2 bonding for (7).

In contrast to the ^1H n.m.r. spectrum of (7), the ^{13}C n.m.r. spectrum reveals 16 distinct carbon signals for the organic ligand at ambient temperature (at 20.7, 27.7, 37.6, 38.2, 49.5, 67.1, 80.4, 83.6, 85.1, 88.0, 90.2, 91.8, 118.6, 121.9, 130.6, and 136.7 p.p.m. downfield of $SiMe_4$) and at 100 °C only two signals (at 38.1 and 82.0 p.p.m.), as a result of coalescence, with the remainder very broadened. Attempts to achieve a fast-exchange limiting spectrum were thwarted by the decomposition of the complex at higher temperatures.

Complex (7) takes up a molecule of carbon monoxide under relatively mild conditions (10 atm, 40 °C) to give pale yellow crystalline $[Ru_2(CO)_6(C_{16}H_{16})]$, whose i.r.

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* Throughout this paper: 1 cal = 4.184 J; 1 atm = 101 325 Pa; 1 Torr = (101 325/760) Pa.

[31] F. A. Cotton, D. L. Hunter, and P. Lahuerta, *J. Amer. Chem. Soc.*, 1975, **97**, 1046.

[32] F. A. Cotton and D. L. Hunter, *J. Amer. Chem. Soc.*, 1975, **97**, 5739.

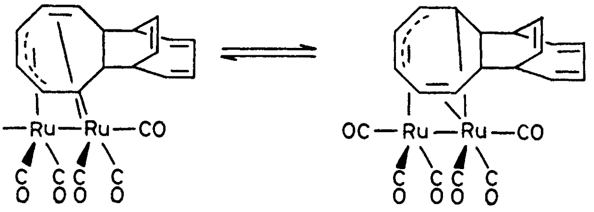
[33] B. E. Mann, *J. Organometallic Chem.*, 1977, **141**, C33; K. J. Karel and M. Brookhart, *J. Amer. Chem. Soc.*, 1978, **100**, 1619.

[34] B. E. Mann, *J.C.S. Chem. Comm.*, 1977, 626.

[35] B. E. Mann and P. M. Maitlis, *J.C.S. Chem. Comm.*, 1976, 1058.

[36] D. Kost, E. H. Carlson, and M. Raban, *J.C.S. Chem. Comm.*, 1971, 656.

spectrum (Table) is nearly identical to that of the cyclo-octatriene complex [Ru$_2$(CO)$_6$(C$_8$H$_{10}$)].[24] This suggests structure (9), in which a partial detachment of the olefin from ruthenium has occurred. As might be expected, warming (9) in hexane effects a rapid regeneration of (7). Moreover, (9) is fluxional, undergoing an apparently identical rearrangement to (7) within the $\eta^1:\eta^2:\eta^3$-bonded ring, (9a) $\rightleftharpoons$ (9b). Once again, the fast-exchange limiting spectrum (*ca.* 20 °C) [τ 4.03 (m, 4 H), 4.28 (m, 2 H), 5.48 (m, 2 H), 5.79 (m, 2 H), 6.88 (m, 2 H), 7.20 (m, 2 H), and 7.76 (m, 2 H)] implies the generation of a time-averaged mirror plane of molecular symmetry. On cooling to *ca.* −20 °C, onset of broadening occurs until at the slow-exchange limit (*ca.* −80 °C) the spectrum [τ 4.10 (m, 6 H), 4.37 (m, 1 H), 5.45 (m, 2 H), 5.84 (m, 1 H), 6.98 (m, 1 H), 7.57 (m, 2 H), 7.90 (m, 1 H), 8.50 (m, 1 H), and 8.70 (m, 1 H)] becomes even more complex than that of the pentacarbonyl (7), allowing no satisfactory assignment.



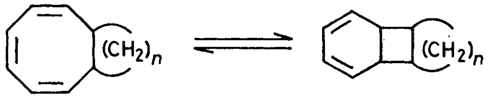
(9a) (9b)

Physical and spectroscopic data for new compounds

Compound	Colour	M.p. (θ_c/°C)	Carbonyl-stretching bands (cm^{-1}) [a]	^{1}H N.m.r. spectrum (τ) [b]
C$_{16}$H$_{16}$ (1a)	White	78—79		4.15 (m, 6 H), 4.35 (m, 4 H), 6.70 (m, 2 H), 7.25 (m, 4 H)
[Ru(CO)$_3$(C$_{16}$H$_{16}$)] (6a)	Pale yellow	115—118	2 061s 1 995s 1 986s	4.28 (m, 8 H), 6.53 (m, 2 H), 7.22 (m, 4 H), 8.34 (m, 2 H)
[Ru$_2$(CO)$_5$(C$_{16}$H$_{16}$)] (7)	Yellow	142—143 (decomp.)	2 062s 2 004s 1 995s 1 980w 1 940m	see Figure 2
[Ru$_2$(CO)$_6$(C$_{16}$H$_{16}$)] (9)	Pale yellow	116 (decomp.)	2 071s 2 035s 2 008s 1 993m 1 977m	4.03 (m, 4 H), 4.28 (m, 2 H), 5.48 (m, 2 H), 5.79 (m, 2 H), 6.88 (m, 2 H), 7.20 (m, 2 H), 7.76 (m, 2 H) [c]
[Ru$_3$H$_2$(CO)$_9$(C$_{16}$H$_{14}$)] (18)	Yellow	136—137 (decomp.)	2 104m 2 075s 2 054s 2 040s 2 025m 2011s 2008s 1984m	4.12 (m, 6 H), 4.67 (dd, 1 H), 5.91 (t, 1 H), 7.03 (m, 4 H), 7.68 (m, 2 H), 27.96 (br, 2 H)
[Fe(CO)$_3$(C$_{16}$H$_{16}$)] (6b)	Pale yellow	130—132	2 046s 1 980s 1 972s	4.25 (m, 6 H), 4.55 (m, 2 H), 6.55 (m, 2 H), 7.17 (m, 4 H), 8.32 (m, 2 H)

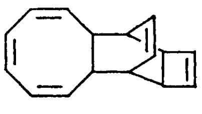
[a] In hexane. [b] In CDCl$_3$. [c] Fluxional molecule (see Discussion section).

The preference of the new dimer of cot for the bicyclo-[4.2.0]octadiene conformation (1a) rather than the tautomeric cyclo-octatriene conformation (1b) is not easily explained, since the factors controlling the relative stabilities of such species are not well understood. Cyclo-octa-1,3,5-triene itself exists in thermal equilibrium [37,38] with its tautomer bicyclo-octa-2,4-diene such that at 80—100 °C the triene : diene ratio is of the order of 6 : 1. On the other hand, for the hydrocarbons (11) and (12) the corresponding ratios are 1 : 32 (at 58 °C) and 1 : 1 (at 114 °C) respectively, while for (10) only the bicyclic form (10a) is detectable. The isolation of the tricarbonylruthenium complex of (1a) and the pentacarbonyldiruthenium complex of the valence tautomer (1b) is strongly reminiscent of the sequestration of the diene and triene tautomers of the bicyclo-octadiene–cyclo-octatriene systems (10)—(12) as complexes of Fe(CO)$_3$ and Mo(CO)$_3$ respectively.[39]



	n	
(10a)	2	(10b)
(11a)	3	(11b)
(12a)	4	(12b)

An attempt to convert (1a) into (1b) with silver ion [40] was unsuccessful. Treatment with Ag[BF$_4$] in acetone did effect a transformation, producing a species with a quite different ^{1}H n.m.r. spectrum [τ 3.52 (dd, *J* 2 and 4 Hz, 2 H), 3.74 (m, 4 H), 3.92 (m, 4 H), 6.65 (m, 4 H), and 7.04 (m, 2 H)], but efforts at isolation were defeated by its rapid reversion to (1a). On the basis of the n.m.r. spectrum, structures (13) or (14) are plausible. The formation of (13) would perhaps more readily account for the reversibility of the change, since thermally allowed electrocyclic ring-opening and -closure processes convert (1b) into (1a) directly. It is interesting to note that (13) is the product to be expected from a Diels–Alder reaction of cot with its bicyclo-octatriene valence tautomer (15).



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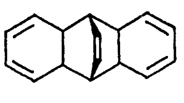

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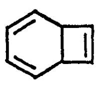

(15)

Hydrogen addition to cot is evident in several of the

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[37] A. C. Cope, *J. Amer. Chem. Soc.*, 1952, **74**, 4867.

[38] R. Huisgen, G. Boche, A. Dahmen, and W. Hechlt, *Tetrahedron Letters*, 1968, 5215.

[39] F. A. Cotton and G. Deganello, *J. Amer. Chem. Soc.*, 1973, **95**, 396.

[40] L. A. Paquette, *Accounts Chem. Res.*, 1971, **4**, 280.

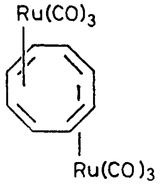
products of the reaction with $[Ru_4H_4(CO)_{12}]$, namely $[Ru(CO)_3(C_8H_{10})]$, $[Ru_2(CO)_6(C_8H_{10})]$, and $[Ru_3(CO)_6(\eta^5\text{-}C_8H_9)(\eta^7\text{-}C_8H_9)]$. Mass and n.m.r. spectra of these complexes prepared from cot and $[Ru_4(^2H)_4(CO)_{12}]$[2] revealed no incorporation of deuterium, so ruling out transfer from the cluster. Hydrogen transfer from the solvent, cot, or water[41] present in the solvent must therefore occur. Incorporation of deuterium into (1a), (6a), or (7) was also not observed.

The new dimer (1a) can be envisaged as the bicyclo[4.2.0]octadiene valence tautomer of the dimer (1b) which would directly arise from a concerted $(4 + 2)\pi$ Diels–Alder self-addition of cot. This self-addition is, however, prohibited by the non-conjugated 'tub' conformation adopted by cot, which does not provide the necessary near-planar 1,3-diene system. Bicyclo[4.2.0]octa-2,4,7-triene (15), which co-exists in low abundance with its valence tautomer cot, does contain such a system and is capable of participating in $(4 + 2)\pi$ cycloadditions. This is witnessed by the formation of adducts of (15) on treatment of cot with dienophiles.[42] Were it to behave in this manner with a molecule of monocyclic cot then (13) would be formed and thence (1a) perhaps. However, extensive studies[42] on the dimerisation of cot have not provided any evidence for the formation of (13), (1a), or (1b). It is therefore apparent that carbonylruthenium complexes are directly involved in the formation of (1a). Moreover, it is attractive to consider that the tricarbonylruthenium complex of cot $[Ru(CO)_3(\eta^4\text{-}C_8H_8)]$ may be important in this respect. Although a classic fluxional[23] molecule, an *X*-ray diffraction study[43] has shown that the instantaneously unco-ordinated 1,3-diene portion of the olefin is very nearly planar, thus in principle allowing its participation in thermal $(4 + 2)\pi$ cycloaddition. Whether involvement is in accordance with this premise is doubtful since several dienophiles have been shown[44,45] to undergo 1,3-addition to $[M(CO)_3(\eta^4\text{-}C_8H_8)]$ (M = Fe or Ru), but that the complex *is* involved seems certain. Treatment of $[Ru(CO)_3(\eta^4\text{-}C_8H_8)]$ with cot under conditions identical to those of the $[Ru_4H_4(CO)_{12}]$ reaction gave (6a) and (7) in 40 and 25% yields respectively, but with no free dimer.

This result suggested that these complexes should also be formed on heating $[Ru_3(CO)_{12}]$ and cot together, a reaction which has been well studied[23,46] and shown to give $[Ru(CO)_3(\eta^4\text{-}C_8H_8)]$ as one of the products. Carrying out the reaction as for $[Ru_4H_4(CO)_{12}]$ did indeed give both (6a) and (7) in comparable yields, again with no free dimer. These two complexes can therefore now be added to the list of previously described products of the reaction of cot with $[Ru_3(CO)_{12}]$: $[Ru(CO)_3(C_8H_8)]$, $[Ru_2(CO)_6(C_8H_8)]$, $[Ru_2(CO)_5(C_8H_8)]$, $[Ru_3(CO)_4(C_8H_8)_2]$, $[Ru_3(CO)_8(C_8H_6)]$,[21] and $[Ru_3(CO)_6(C_8H_9)_2]$.[22] Cotton *et al.*[23] did describe the isolation from $[Ru_3(CO)_{12}]$ and cot of a pale yellow crystalline material in low yield, tentatively formulated as *trans*-$[\{Ru(CO)_3\}_2(C_8H_8)]$ (16) on the basis of its tricarbonyl i.r. spectrum [ν(CO) in heptane at 2 067s, 2 000s, and 1 992s cm^{-1}]. This spectrum is similar to that of (6a) (Table) and the complex is described as separating from the other products on chromatography exactly as does (6a) in our hands, so it seems that the complex probably is (6a).

Confirmation that the production of complexes (6a) and (7) from $[Ru(CO)_3(\eta^4\text{-}C_8H_8)]$ and cot is induced thermally was obtained by u.v. irradiation of the reactants in heptane solution. Under these conditions only $[Ru_2(CO)_5(C_8H_8)]$ and $[Ru_3(CO)_4(C_8H_8)_2]$ were formed.

Further support for the existence of $[Ru(CO)_3(\eta^4\text{-}C_8H_8)]$ as a precursor of (6a) and (7) comes from a series of reactions which eliminate other possibilities. Heating $[Ru_2(CO)_5(C_8H_8)]$ or $[Ru_2(CO)_6(C_8H_8)]$ with cot, and (6a) with $[Ru_3(CO)_{12}]$ or $[Ru_4H_4(CO)_{12}]$, did not lead to (7). The reactions of $[Ru_3(CO)_{12}]$ and $[Ru_4H_4(CO)_{12}]$ with (1a) likewise failed to give (7) although each cluster did afford (6a) in *ca.* 30% yield. From $[Ru_3(CO)_{12}]$ a low-yield product was obtained in addition, yellow crystals formulated as $[Ru_3H_2(CO)_9(C_{16}H_{14})]$. The striking similarity of the i.r. spectrum (Table) with that of $[Ru_3H_2(CO)_9(C_8H_{12})]$[18] (17) [$\nu$(CO) at 2 105m, 2 076s, 2 054vs, 2 040s, 2 026m, 2 013s, 2 006m, and 1 987m cm^{-1}] suggests a closely related structure, while the broad high-field ^{1}H n.m.r. signal confirms the existence of two fluxional bridging hydride ligands, undergoing the mutual exchange common to such species. The observation of eight olefinic and six aliphatic proton resonances



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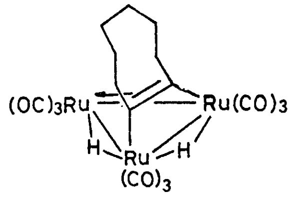

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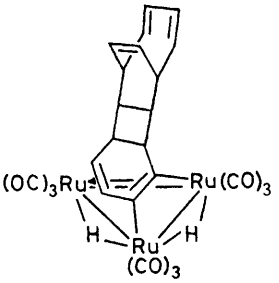
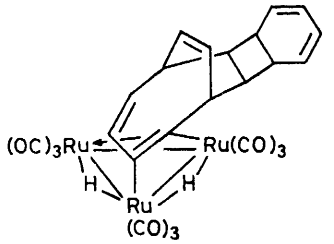


(18a)



(18b)

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

[42] G. I. Fray and R. G. Saxton, 'The Chemistry of Cyclooctatetraene and its Derivatives,' Cambridge University Press, 1978.

[43] F. A. Cotton and R. Eiss, *J. Amer. Chem. Soc.*, 1969, **91**, 6593.

[44] J. Weaver and P. Woodward, *J. Chem. Soc.* (*A*), 1971, 3521.

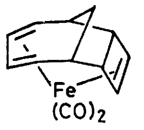
[45] M. Green, S. Heathcock, and D. C. Wood, *J.C.S. Dalton*, 1973, 1564.

[46] M. I. Bruce, M. Cooke, and M. Green, *J. Organometallic Chem.*, 1968, **13**, 227.

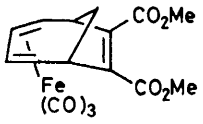
indicates that the complex contains the new dimer in its bicyclo-octadiene tautomeric form, co-ordinated either as in (18a) or (18b).

There is thus strong evidence that the new dimer (1a) and its carbonylruthenium complexes are formed *via* the thermal reaction of cot with $[Ru(CO)_3(\eta^4\text{-}C_8H_8)]$. An insight into the actual mechanism of the reaction is provided by the *X*-ray diffraction studies [20,28] on (6a) and (7). These have shown that in each complex the $C_{16}H_{16}$ hydrocarbon is in a conformation such that the hydrogen atoms on the 1,2 carbons linking the two C_8 rings are *cis* with respect to one another and *exo* with respect to the metal. This at once suggests that an attacking cot ring approaches the co-ordinated ring of $[Ru(CO)_3(\eta^4\text{-}C_8H_8)]$ on the same side as the metal, which in turn implies pre-co-ordination to the metal since in its absence steric factors would surely favour *exo* attack.

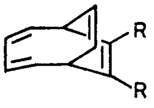
We are thus drawn to the conclusion that complex (6a) is formed through a $[Ru(CO)_3(\eta^4\text{-}C_8H_8)]$ molecule being attacked at ruthenium by a cot molecule which is subsequently transferred to the original ring in an intramolecular manner. Wide precedent exists for such metal participation, or a template effect. Particularly relevant are Pettit's demonstrations [47,48] that a variety of carbonyliron complexes of olefins react with olefins or acetylenes to give products whose structures are consistent with metal involvement in the linking of the hydrocarbons. For example, tricarbonyl-cyclobutadieneiron and -cycloheptatrieneiron react under u.v. irradiation with cycloheptatriene and $MeO_2CC{\equiv}CCO_2Me$ respectively to afford the complexes (19) [47] and (20).[48]



(19)



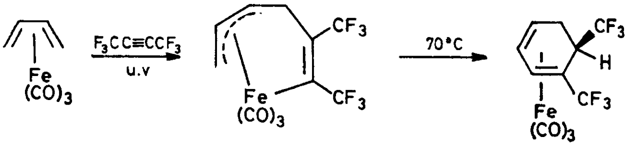
(20)



(21)

The structure of the latter, determinated by *X*-ray diffraction, significantly has the acetylene attached to the same face of the triene as iron. As in our own studies, free hydrocarbons were also produced. Thus, irradiation of $[Fe(CO)_3(\eta^4\text{-}C_8H_8)]$ with $RC{\equiv}CR$ ($R = CO_2Me$ or Ph) provided (21) in *ca.* 20% yield, a reaction also known [49] to proceed thermally. The formation of (20) and (21) is viewed by Pettit as resulting from a concerted $(6 + 2)\pi$ cycloaddition, normally ' forbidden ' in the Woodward–Hoffmann sense but now ' allowed ' through metal participation. Evidence is, however, accumulating in favour of a stepwise rather than a concerted mechanism for such template processes. Prominent among this is the isolation of an intermediate (22) in the formal Diels–Alder addition of hexafluorobut-2-yne to butadienetricarbonyliron.[50] For this reason we favour a stepwise mechanism for the linking of the two cot molecules by carbonylruthenium complexes.

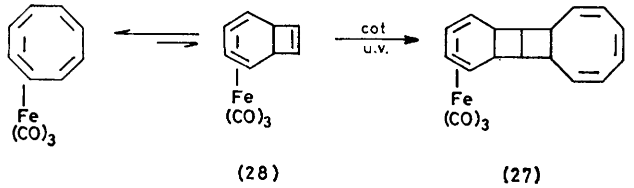
There are several paths which can be devised for the linking, of which perhaps the most plausible, although still tentative, is that in Scheme 1. This envisages the initial generation from $[Ru(CO)_3(\eta^4\text{-}C_8H_8)]$ of the complex $[Ru(CO)_3(\eta^2\text{-}C_8H_8)_2]$,[51] which rearranges to an allylic complex (24) in which one cot ring is σ-bonded to both ruthenium and the other ring. Subsequent formation of a second new carbon–carbon bond in (25), an $Ru(CO)_3$ migration to give (26), and ring closure provides (6a) with the requisite conformation of the $C_{16}H_{16}$ ligand.



(22)

The path by which the diruthenium complex (7) is formed from $[Ru(CO)_3(\eta^4\text{-}C_8H_8)]$ remains obscure. An apparently obvious route is that in which (6a) co-ordinates an $Ru(CO)_3$ group to the uncomplexed diene unit, then eliminates a carbonyl ligand during metal–metal bond formation. Treatment of (6a) with $[Ru_3(CO)_{12}]$ did not, however, yield any (7). The source of free (1a) in the reaction of cot with $[Ru_4H_4(CO)_{12}]$ is likewise unclear since the reaction between cot and $[Ru(CO)_3(\eta^4\text{-}C_8H_8)]$ gave (6a) and (7) apparently cleanly, as did that between cot and $[Ru_3(CO)_{12}]$. Small amounts of free (1a) would not easily be detected and some may have been formed in these reactions. Nevertheless, the high yield of uncomplexed (1a) produced from $[Ru_4H_4(CO)_{12}]$ is unique and unexplained.

The reaction of cot with $[Fe(CO)_3(\eta^4\text{-}C_8H_8)]$ in heptane at reflux provides an interesting contrast to that with isostructural $[Ru(CO)_3(\eta^4\text{-}C_8H_8)]$. The sole product $[Fe(CO)_3(C_{16}H_{16})]$ is again a complex of a cot dimer, but the ^1H n.m.r. spectrum reveals a different mode of dimerisation with iron, in identifying the complex as of formulation (27). The photochemically induced reactions of $[Fe(CO)_5]$ and $[Fe(CO)_3(\eta^4\text{-}C_8H_8)]$ with cot have been previously investigated [52] and observed to yield a series of carbonyliron complexes derived from the cot dimers (2) and (3). Among these was (27), a deriv-



(28) (27)

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[47] J. S. Ward and R. Pettit, *J. Amer. Chem. Soc.*, 1971, **93**, 262.

[48] R. E. Davis, T. A. Dodds, T.-H. Hseu, J. C. Wagnon, T. Devon, J. Tancrede, J. S. McKennis, and R. Pettit, *J. Amer. Chem. Soc.*, 1974, **96**, 7562.

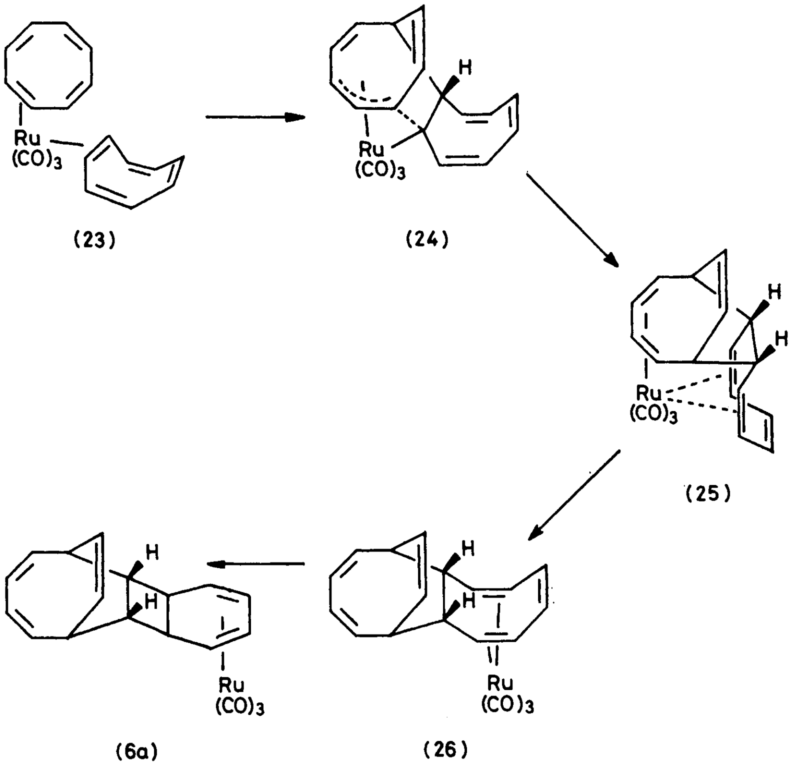
[49] U. Kruerke, *Angew. Chem. Internat. Edn.*, 1967, **6**, 79.

[50] R. Davis, M. Green, and R. P. Hughes, *J.C.S. Chem. Comm.*, 1975, 405.

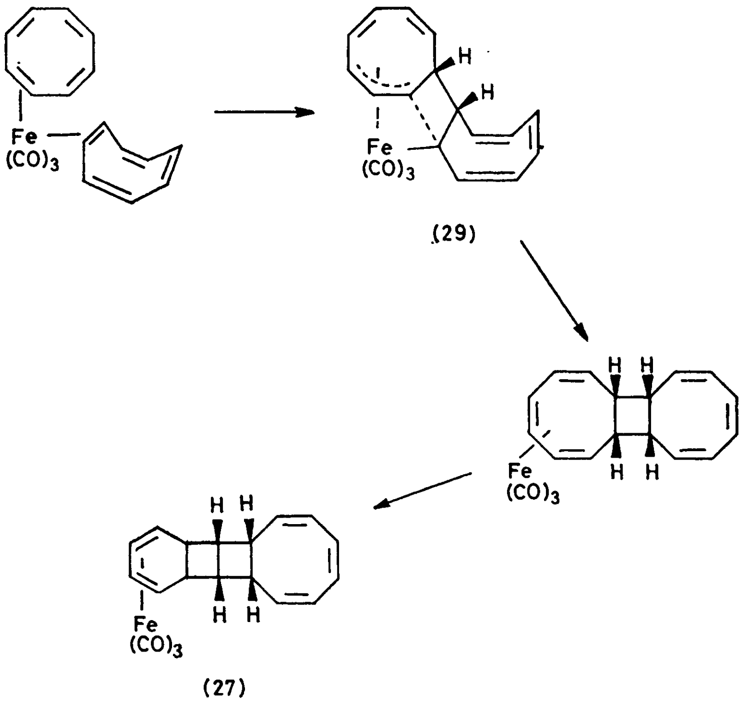
[51] I. B. Benson, S. A. R. Knox, R. F. D. Stansfield, and P. Woodward, *J.C.S. Chem. Comm.*, 1977, 404.

[52] G. N. Schrauzer and P. W. Glockner, *J. Amer. Chem. Soc.*, 1968, **90**, 2800.

ative of the bicyclo-octadiene valence tautomer of dimer (2). The photochemical production of (27) led the earlier workers to propose[52] a $(2 + 2)\pi$ cycloaddition process involving the tricarbonyliron complex (28). Our demonstration that (27) is formed specifically under thermal conditions encourages consideration of a template mechanism related to that in Scheme 1. One such mechanism (Scheme 2) generates a cot dimer with the indicated bridgehead hydrogen atoms *cis* relative to one another and *exo* with respect to the metal. This is



SCHEME 1



SCHEME 2

exactly the conformation which is revealed in an *X*-ray diffraction study of (27).[53]

It is fascinating that in the thermal reactions of cot with $[M(CO)_3(\eta^4\text{-}C_8H_8)]$ ruthenium induces formally $(4 + 2)\pi$ dimerisation of cot and iron formally $(2 + 2)\pi$ dimerisation. In terms of the tentatively proposed mechanisms (Schemes 1 and 2) this variation is attributed to a different geometry of the $\sigma : \eta^3$-bonded intermediates (24) and (29), with the two metals adopting different allylic bonding sites. Evidence that this is not overly speculative is provided by studies on the protonation of $[M(CO)_3(\eta^4\text{-}C_8H_8)]$, which have shown that iron and ruthenium tricarbonyl groups do vary in their modes of bonding to a $[C_8H_9]^+$ hydrocarbon.[54] Such a hydrocarbon is not unrelated to that within (24) or (29).

The iron complex (6b) of the new dimer of cot is not produced in any known reaction of $[Fe(CO)_5]$ or $[Fe(CO)_3(\eta^4\text{-}C_8H_8)]$ with cot. Treatment of $[Fe_2(CO)_9]$ with (1a) in tetrahydrofuran at room temperature did, however, afford a good yield of (6b), whose identity was clearly revealed by the similarity of the ^{1}H n.m.r. spectrum to that of (6a).

EXPERIMENTAL

Infrared spectra were recorded with a Perkin-Elmer 257 spectrometer, using calcium fluoride cells of 1.0-mm path length, and were calibrated *via* the absorption at 1 601 cm^{-1} of polystyrene. N.m.r. spectra were obtained using JEOL PFT-100 and Varian Associates HA 100 instruments and mass spectra with an A.E.I. MS 902 spectrometer. Reactions were performed under a nitrogen atmosphere, employing solvents dried by distillation from calcium hydride. Silica gel (100—200 mesh) or alumina (Brockman Activity II) columns (50 × 2 cm) were used in chromatography. The u.v. radiation source was a 250-W mercury-vapour lamp. Cyclo-octatetraene purchased from B.A.S.F. was distilled immediately prior to use. Literature methods were used in the preparations of $[Ru_4H_4(CO)_{12}]$ [2] and $[Ru(CO)_3(\eta^4\text{-}C_8H_8)]$.[55] The complex $[Ru_2(CO)_6(C_8H_8)]$ was obtained in quantitative yield by autoclave carbonylation (20 atm, acetone, 60 °C, 10 h) of $[Ru_2(CO)_5(C_8H_8)]$. Spectroscopic and physical data for new compounds are collected in the Table.

The Reaction of $[Ru_4H_4(CO)_{12}]$ *with* cot.—A mixture of $[Ru_4H_4(CO)_{12}]$ (1.0 g, 1.34 mmol) and cot (6.0 g, 57.7 mmol) was heated in heptane (150 cm^3) under reflux for 20 h, producing a very dark red solution. Solvent and unchanged cot were then evaporated at reduced pressure and the red residue chromatographed on silica gel. Elution with hexane or hexane–dichloromethane mixtures developed eight bands.

Band 1 (yellow, eluted with hexane) gave 15 mg (1%) of a yellow oil, purified by distillation (25 °C, 10^{-2} Torr) and identified as the known [24] cyclo-octatriene complex $[Ru(CO)_3(C_8H_{10})]$ by i.r. and mass spectra. Band 2 (yellow, eluted with hexane) gave 10 mg (1%) of a pale yellow solid, identified as the known [24] cyclo-octatriene complex $[Ru_2(CO)_6(C_8H_{10})]$ by i.r. and mass spectra. Band 3 [pink, eluted with dichloromethane–hexane (1 : 9)] gave a pink crystalline mass composed of $C_{16}H_{16}$ (1a) (predominantly) and $[Ru(CO)_3(C_{16}H_{16})]$ (6a), the latter being identified by its i.r. spectrum. Heating this mixture in benzene (150 cm^3) at reflux with $NMe_3O\cdot 2H_2O$ (1.5 g) for 1 h gave a very dark solution. Removal of solvent and sublimation (100 °C, 10^{-2} Torr) to a water-cooled probe then yielded *ca.* 300 mg of white crystalline $C_{16}H_{16}$ (Found: C, 92.1; H, 7.8%; *M* 208. $C_{16}H_{16}$ requires C, 92.3; H, 7.7%; *M* 208). Band 4 [yellow, eluted with dichloromethane–hexane (1 : 3)] gave 30 mg (2%) of yellow crystalline $[Ru_2(CO)_5(C_{16}H_{16})]$ (7) (Found: C, 45.7; H, 3.0%; *M* 551. $C_{21}H_{16}O_5Ru_2$ requires C, 45.8; H, 2.9%; *M* 551) on recrystallisation from hexane. Band 5 [green, eluted with dichloromethane–hexane (1 : 3)] gave 12 mg of red-green dichroic crystals, as yet unidentified. Band 6 [pale yellow, eluted with dichloromethane–hexane (1 : 3)] gave 10 mg (1%) of the known [21] yellow crystalline pentalene complex $[Ru_3(CO)_8(C_8H_6)]$, identified by i.r., n.m.r., and mass spectra. Band 7 [red, eluted with dichloromethane–hexane (2 : 3)] gave 35 mg (3%) of the known [22] dark red crystalline $[Ru_3(CO)_6(\eta^5\text{-}C_8H_9)(\eta^7\text{-}C_8H_9)]$, identified by i.r., n.m.r., and mass spectra. Band 8 [orange, eluted with dichloromethane–hexane (2 : 3)] gave 16 mg (2%) of the known [23] orange $[Ru_2(CO)_5(C_8H_8)]$, identified by i.r., n.m.r., and mass spectra.

The Reaction of $[Ru_3(CO)_{12}]$ *with* cot.—After heating $[Ru_3(CO)_{12}]$ (2.0 g, 3.1 mmol) and cot (7.5 g, 72.1 mmol) in heptane (150 cm^3) under reflux for 17 h the resulting solution was treated as above. Chromatography, eluting with hexane, gave $[Ru(CO)_3(C_8H_{10})]$ (25 mg, 1%),[24] $[Ru_2(CO)_6(C_8H_{10})]$ (15 mg, 1%),[24] and a pale yellow band which provided 0.37 g (10%) of pale yellow crystalline $[Ru(CO)_3(C_{16}H_{16})]$ (6a) (Found: C, 58.2; H, 4.1%; *M* 394. $C_{19}H_{16}O_3Ru$ requires C, 58.0; H, 4.1%; *M* 394). Further elution with dichloromethane–hexane (1 : 3) developed two yellow bands, providing in turn 0.105 g (4%) of $[Ru_2(CO)_5(C_{16}H_{16})]$ (7) and 15 mg (1%) of $[Ru_3(CO)_8(C_8H_6)]$.[21] Finally, dichloromethane–hexane (2 : 3) removed an orange band yielding 1.59 g (76%) of $[Ru_2(CO)_5(C_8H_8)]$.[23] Each complex was identified by i.r. and n.m.r. spectra.

The Reaction of $[Ru(CO)_3(C_{16}H_{16})]$ (6a) *with* NMe_3O.—Excess of $NMe_3O\cdot 2H_2O$ (1.13 g, 10.2 mmol) was added to a benzene (150 cm^3) solution of (6a) (0.5 g, 1.27 mmol) which was heated under reflux for 1 h. The pale yellow solution became very dark and after cooling was filtered and evaporated under reduced pressure. Sublimation of the residue (100 °C, 10^{-2} Torr) to a water-cooled probe then gave 0.25 g (94%) of white crystalline $C_{16}H_{16}$ (1a).

Reactions of $C_{16}H_{16}$ (1a).—(*a*) *With* $[Ru_4H_4(CO)_{12}]$. The dimer (0.1 g, 0.48 mmol) was heated in heptane (100 cm^3) under reflux with $[Ru_4H_4(CO)_{12}]$ (0.1 g, 0.13 mmol) for 2.5 h. Chromatography, eluting with dichloromethane–hexane (1 : 3), then gave 68 mg (32%) of yellow crystalline $[Ru(CO)_3(C_{16}H_{16})]$ (6a).

(*b*) *With* $[Ru_3(CO)_{12}]$. The dimer (0.1 g, 0.48 mmol) was heated in heptane (100 cm^3) under reflux with $[Ru_3(CO)_{12}]$ (0.15 g, 0.24 mmol) for 2 h. Chromatography of the mixture provided four bands. Elution of the first with hexane returned 35 mg of unchanged $[Ru_3(CO)_{12}]$. Elution of the second with dichloromethane–hexane (1 : 9) yielded yellow crystals, shown by i.r. to contain $[Ru(CO)_3(C_{16}H_{16})]$ (6a) and a new compound. Crystallisation from hexane efficiently separated these into 82 mg (30%) of (6a) and 12 mg (7%) of yellow crystalline $[Ru_3H_2(CO)_9(C_{16}H_{14})]$ (18) (Found: C, 39.3; H, 2.1%; *M* 765. $C_{25}H_{16}O_9Ru_3$ requires

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[53] A. Robson and M. R. Truter, *J. Chem. Soc.* (*A*), 1968, 3079.

[54] A. D. Charles, P. Diversi, B. F. G. Johnson, and J. Lewis, *J. Organometallic Chem.*, 1976, **116**, C25 and refs. therein.

[55] F. A. Cotton and D. L. Hunter, *J. Amer. Chem. Soc.*, 1976, **98**, 1413.

C, 39.3; H, 2.1%; *M* 765). The remaining bands, orange and yellow, were eluted with dichloromethane–hexane (2 : 3), but contained only small amounts of unidentified material.

(*c*) *With* [$Fe_2(CO)_9$]. The dimer (0.11 g, 0.53 mmol) and [$Fe_2(CO)_9$] (1.0 g, 2.75 mmol) were stirred together in tetrahydrofuran (thf) (50 cm^3) at room temperature for 17 h. Removal of solvent and [$Fe(CO)_5$] at reduced pressure, followed by chromatography of the residue on alumina, eluting with dichloromethane–hexane (1 : 4), gave (82 mg, 45%) yellow crystals of [$Fe(CO)_3(C_{16}H_{16})$] (6b) (Found: C, 65.4; H, 4.6%; *M* 348. $C_{19}H_{16}FeO_3$ requires C, 65.5; H, 4.6%; *M* 348).

(*d*) *With* Ag[BF_4]. Following addition of Ag[BF_4] (0.3 g, 1.54 mmol) to a solution of (1a) (90 mg, 0.43 mmol) in $(CD_3)_2CO$ (5 cm^3), the mixture was stirred for 1 h, after which time a ^1H n.m.r. spectrum indicated reaction was complete. After filtration and evaporation of solvent a white waxy solid was obtained (see Discussion section), but on sublimation (100 °C, 10^{-2} Torr) to a water-cooled probe only the original dimer was isolated.

The Reaction of [$Ru_2(CO)_5(C_{16}H_{16})$] (7) *with* CO.—Autoclave carbonylation (10 atm) of an acetone (25 cm^3) solution of (7) (0.1 g, 0.18 mmol) at 40 °C for 10 h, followed by evaporation of solvent and chromatography of the residue, afforded two yellow bands. Elution of the first with hexane gave a trace amount of [$Ru_3(CO)_{12}$], and of the second with dichloromethane–hexane (1 : 4) gave 65 mg (62%) of pale yellow crystalline [$Ru_2(CO)_6(C_{16}H_{16})$] (9) (Found: C, 44.9; H, 2.8%; *M* 579. $C_{22}H_{16}O_6Ru_2$ requires C, 45.7; H, 2.8%; *M* 579).

Reactions of [$M(CO)_3(\eta^4\text{-}C_8H_8)$] *with* cot.—(*a*) [$Ru(CO)_3(\eta^4\text{-}C_8H_8)$]. A heptane (25 cm^3) solution of [$Ru(CO)_3(\eta^4\text{-}C_8H_8)$] (0.25 g, 0.87 mmol) and cot (5.0 g, 48.1 mmol) was heated under reflux and the course of reaction monitored by i.r. spectroscopy. Reaction was complete after 9 h. Solvent and excess of cot were evaporated off and the residue chromatographed on silica gel. Elution with dichloromethane–hexane (1 : 3) developed three yellow bands. The first contained only cot, with the second and third providing 0.15 g (40%) of [$Ru(CO)_3(C_{16}H_{16})$] (6a) and 61 mg (25%) of [$Ru_2(CO)_5(C_{16}H_{16})$] (7) respectively, identified by their i.r. spectra.

(*b*) [$Fe(CO)_3(\eta^4\text{-}C_8H_8)$]. A heptane (50 cm^3) solution of [$Fe(CO)_3(\eta^4\text{-}C_8H_8)$] (1.0 g, 4.1 mmol) and cot (12.0 g, 115 mmol) was heated under reflux for 2 d, after which time i.r. spectra indicated the reaction to be complete. Chromatography on alumina, eluting with dichloromethane–hexane (1 : 3), developed what appeared to be overlapping yellow and orange bands. These were removed together and solvent evaporated to give a mixture of red and yellow crystals. Washing with hexane readily dissolved the red material, identified by i.r. as [$Fe(CO)_3(\eta^4\text{-}C_8H_8)$], leaving 0.39 g (24%) of [$Fe(CO)_3(C_{16}H_{16})$] (27) (Found: C, 65.3; H, 4.8%; *M* 348. $C_{19}H_{16}FeO_3$ requires C, 65.5; H, 4.6%; *M* 348), further identified by comparison of its i.r. and ^1H n.m.r. spectra and m.p. (Found: 169 °C; lit.,[52] 172 °C) with those reported.[52]

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