Reactivity of Co-ordinated Ligands. Part XVI.[1] The Reaction of Bicyclo[3.2.1]octa-2,6-diene with Dodecacarbonyltriruthenium

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The complexes $C_8H_{10}Ru(CO)_3$ (1) and $C_{16}H_{20}Ru(CO)_3$ (2) have been prepared from the reaction of bicyclo[3.2.1]-octa-2,6-diene (C_8H_{10}) with dodecacarbonyltriruthenium in benzene under reflux. Complex (1) was characterised as (2—4,6-η-bicyclo[3.2.1]octadiene)tricarbonylruthenium on the basis of ^1H n.m.r. spectroscopic data. This complex undergoes hydride-ion abstraction with Ph_3CBF_4 to yield the monocationic complex [(2—4,6,7-η-C_8H_9)-$Ru(CO)_3$]BF_4. Treatment of this complex with $NaBH_4$ yields the initial complex (1). Two possible mechanisms for the formation of complex (1) have been considered; ^1H n.m.r. data on the complex derived from 2—4,6-η-C_8H_9D suggest that the mechanism involves co-ordination of the diene followed by H migration *via* the metal rather than a bond-breaking mechanism.

WE have previously reported [2] that tricarbonyl(cyclo-octa-1,5-diene)ruthenium readily undergoes thermal conversion into its 1—3,6-η-isomer, which is also the product of hydride attack on the complex cation [(1—3,5,6-η-C_8H_{11})Ru(CO)$_3$]$^+$. In the latter reaction attack of the hydride ion occurs specifically at the C-5 olefinic carbon which is in contrast to the behaviour of the corresponding iron species where attack also occurs at the C-3 allylic carbon.[3] The chemistry of these iron and ruthenium cations contrasts with that of the isoelectronic cations of cobalt and rhodium [(1—3,5,6-η-C_8H_{11})M(π-C_5H_5)]$^+$ (M = Co or Rh), where borohydride attack occurs solely at C-3 to regenerate the 1,5-diene complexes.[4,5] It was to gain further insight into the suspected tendency of (diolefin)Ru(CO)$_3$ complexes to undergo intramolecular oxidative–addition reactions to form stable d^6 metal complexes and to study the mechanism by which such reactions take place that the reaction of bicyclo[3.1.2]-octa-2,6-diene with dodecacarbonyltriruthenium was investigated.

[1] Part XV, *J.C.S. Dalton*, 1973, 404.
[2] A. J. P. Domingos, B. F. G. Johnson, and J. Lewis, unpublished work.
[3] F. A. Cotton, A. J. Deeming, P. L. Josty, S. S. Ullah, A. J. P. Domingos, B. F. G. Johnson, and J. Lewis, *J. Amer. Chem. Soc.*, 1971, **93**, 4624.
[4] J. Lewis and A. W. Parkins, *J. Chem. Soc.* (*A*), 1967, 1150.
[5] J. Evans, B. F. G. Johnson, and J. Lewis, *Chem. Comm.*, 1971, 1252.

RESULTS AND DISCUSSION

Addition of bicyclo[3.2.1]octa-2,6-diene to a benzene solution of $Ru_3(CO)_{12}$ under reflux yields, after chromatography on silica, the complexes $(2—4,6-\eta$-bicyclo[3.2.1]-octadiene)tricarbonylruthenium (1) (a colourless oil, m.p. -10 °C), and $(C_{16}H_{20})Ru(CO)_3$ (2) (yellow crystals). The reaction was also monitored by following the change of i.r. spectrum with time. After 25 h the C–O stretching region of the spectrum exhibits eight sharp bands none of which corresponds to the ruthenium carbonyl. Over more extended periods two other bands appear at 2067 and 1999 cm^{-1} and after ca. 50 h of reaction the spectrum contains two bands which are identical to those of $(1—3,6-\eta-C_8H_{12})Ru(CO)_3$ [2] and suggests that the bicyclic ligand is bonded to a $Ru(CO)_3$ unit through a π-allyl and a carbon–metal σ-bond. The mass spectrum exhibits the isotopic patterns for the molecular ion and for the ions resulting from the successive loss of three carbonyls $(C_8H_{10})Ru(CO)_n{}^+$ $(n = 3—0)$. Other peaks in the spectrum are those corresponding to the fragment ions Ru$^+$ and $C_6H_6Ru^+$. The ^1H n.m.r. spectrum of (1) in deuteriobenzene may be readily interpreted in terms of the proposed structure (Figure 1). The assignments

1-H	τ 7·86
2-H	τ 5·02
3-H	τ 5·78
4-H	τ 6·13
5-H	τ 7·35
6-H, 2(8-H)	τ 9·1—9·4
2(7-H)	τ 8·17
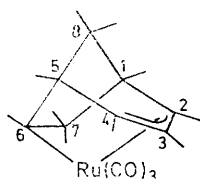
$J_{12} = J_{23} = J_{34} = J_{45} = 6\cdot0$ Hz
$J_{24} = 2\cdot5$ Hz
$J_{17} \sim J_{18} \sim 2$ Hz
$J_{58} = 6$ Hz

FIGURE 1 ^1H N.m.r. data for $(2—4,6-\eta-C_8H_{10})Ru(CO)_3$ in C_6D_6

given were based on double-irradiation experiments. Thus the 2-H triplet of doublets at τ 5·02 (2-H) changed to a triplet on irradiation at 4-H and to a broad doublet on irradiation at 1-H; 3-H changed to a doublet on irradiation at 2-H; the 4-H triplet of doublets gives a triplet on irradiation at 2-H and is changed to a broad doublet on irradiation at 5-H; the 5-H quartet changes to a broad triplet on irradiation at 4-H and to a broad doublet on irradiation at the τ 9·1—9·4 multiplet; the 1-H multiplet gives a broad singlet, a broad doublet, and another broad doublet on irradiations at respectively 2-H, 2(7-H) and 6-H $+2(8\text{-H})$; the 2(7-H) absorption becomes sharper on irradiation at τ 9·1—9·4; the 6-H $+ 2(8\text{-H})$ multiplet is modified by irradiation at 5-H, 1-H, or 2(7-H). Further confirmation of this assignment was obtained from the ^1H n.m.r. spectra of the 3-^2H and $exo\text{-}7\text{-}^2H$ derivatives of complex (1). In the ^1H n.m.r. spectrum of the 3-^2H derivative the 3-H absorption collapsed and the 2-H and 4-H absorptions changed to doublets of doublets, the other absorptions remained identical to those of (1). The

spectrum of the $exo\text{-}7\text{-}^2H$ derivative differs from the spectrum of the non-deuteriated complex only in that the τ 8·17 absorption 2(7-H) corresponds to one proton instead of two, and that some coupling disappears from the multiplets at τ 7·86 (1-H) and τ 9·1—9·4 [6-H $+$ 2(8-H)]. This locates the 6-H proton on the low field side of the τ 9·1—9·4 multiplet. In contrast to the complex $(1—3,6-\eta-C_8H_{12})Ru(CO)_3$, where the two 'outer' allylic protons are equivalent, in the $(2—4,6-\eta-C_8H_{10})Ru(CO)_3$ molecule there exists no plane of symmetry perpendicular to the allylic fragment and this is expressed by the non-equivalence of the chemical shifts of the 'outer' allylic protons. In addition, these protons are coupled by 2·5 Hz in (1), whereas in $(1—3,6-\eta-C_8H_{12})Ru(CO)_3$ no such coupling occurs.

The C–O stretching region of the infrared spectrum of $(C_{16}H_{20})Ru(CO)_3$ (2), which exhibits three sharp bands at 2067, 1999, and 1994 cm^{-1} (n-heptane), is consistent with the existence of a $Ru(CO)_3$ unit in the molecule. This is also supported by the mass spectrum, in which the peaks $(C_{16}H_{20})Ru(CO)_n{}^+$ $(n = 3—0)$ indicate the successive loss of three carbonyls from the molecular ion. Other peaks in the spectrum are those corresponding to $(C_{16}H_{18})Ru(CO)^+$, $(C_{16}H_{18})Ru^+$, $C_{10}H_{12}{}^-Ru^+$, and $C_6H_6Ru^+$. The absence of peaks (C_8H_{10})-$Ru(CO)_n{}^+$ favours the $(C_{16}H_{20})Ru(CO)_3$ formulation of (2), as opposed to $(C_8H_{10})_2Ru(CO)_3$. The ^1H n.m.r. spectrum of complex (2) presents bands of relative intensities $1 : 1 : 1 : 1 : 1 : 15$ at τ 3·86, 4·46, 5·07, 6·27, and 7·0—9·4. The τ 3·86 and 4·46 broad multiplets, besides occurring at nearly the same chemical shifts as the 2-H and 3-H olefinic protons of the non-co-ordinated C_8H_{10} bicyclic diene,[6] have line shapes similar to those of 2-H and 3-H. This suggests that in complex (2) the $C_{16}H_{20}$ moiety has a non-co-ordinated carbon-carbon double-bond in approximately the same environment as the $C(2)=C(3)$ double bond in bicyclo-[3.2.1]octa-2,6-diene. Double-irradiation experiments indicate that the τ 5·07 triplet of doublets, the τ 5·68 triplet, and the τ 6·27 triplet of doublets arise from protons of an allyl fragment π-bonded to the metal, and that each of the two 'outer' allylic protons is coupled to only one proton of the τ 7·0—9·4 complex multiplet. Because of its complexity in the methylene region, no other conclusions can be drawn from the spectrum. The possible structure of (2) is given in Figure 2.
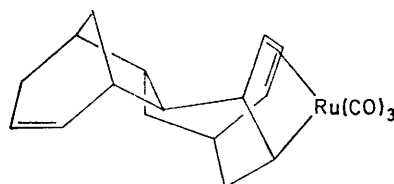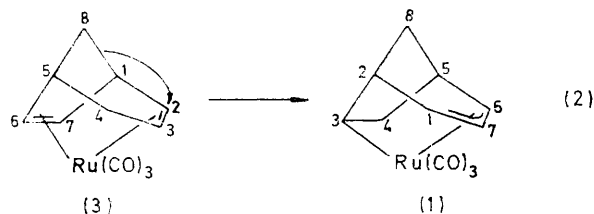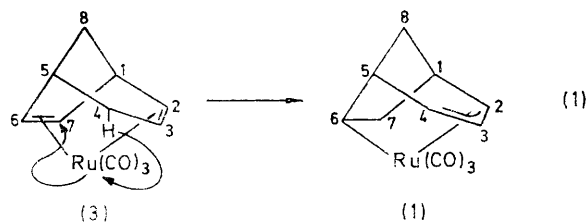

FIGURE 2   Possible structure of $(C_{16}H_{20})Ru(CO)_3$

As $(2—4, 6-\eta-C_8H_{10})Ru(CO)_3$, (1), was isolated from the reaction of the bicyclic diene and $Ru_3(CO)_{12}$, it is reasonable to assume that its production was preceded

6 W. R. Moore, W. R. Moser, and J. E. La Prade, J. Org. Chem., 1963, 28, 2200.

by the formation of the diolefin complex (2,3,6,7-η-C_8H_{10})Ru(CO)$_3$, (3), which then isomerized to (1).


This isomerization can be visualized as occurring by one of two different routes: (1) a hydride transfer or (2) a 1 : 2 carbon–carbon bond shift. The first is similar
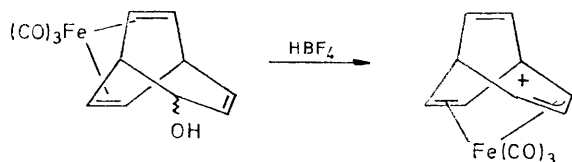
to that proposed for the conversion of (1,5-C_8H_{12})-Ru(CO)$_3$ into the 1—3,6-η-isomer.[2] The rearrangement of the organic ligand in the preparation of a
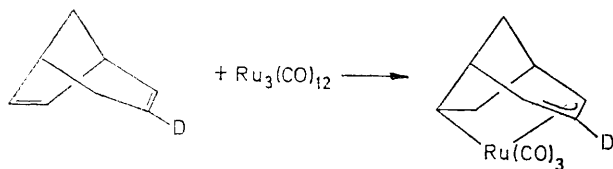
bicyclo[3.2.2]nonadienyltricarbonyliron cation was recently described.[7] In order to differentiate between
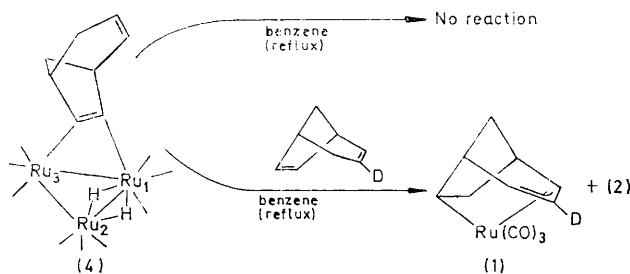
these two mechanisms, the C-3 carbon of bicyclo[3.2.1]-octa-2,6-diene was labelled with deuterium (80% deuteriation) and the diolefin reacted with Ru$_3$(CO)$_{12}$. The ^{1}H n.m.r. spectrum of the complex (2—4,6-η-C_8H_9D)Ru(CO)$_3$ isolated from the reaction differs from the spectrum of the non-deuteriated complex

(Figure 1) only in that the 3-H absorption integrates to 0·2 protons instead of 1, and that the 2-H and 4-H bands are doublets of doublets as a result of the loss of the coupling to the central allylic proton. Hence, if the assumption that complex (1) is formed from (3) is correct, this conversion proceeds by a hydride-transfer mechanism.

In order to gain further insight into the process of formation of complex (1), bicyclo[3.2.1]octa-2,6-diene was treated with Ru$_3$(CO)$_{12}$ and the reaction, which was monitored by following the change in i.r. spectrum, was stopped when the intermediate (which exhibits eight C–O stretching vibrations in its infrared spectrum) attained its maximum concentration (ca. 25 h). This intermediate was isolated and characterised as H$_2$-(C_8H_8)Ru$_3$(CO)$_9$, (4) on the basis of its ^{1}H n.m.r. spectrum. The formation of this molecule requires that two hydrogen atoms are removed from the C(6)=C(7) olefin to form two non-equivalent metalhydrides. The remaining organic moiety C_8H_8 is complexed to the metal cluster by two metal–carbon σ-bonds and one metal–olefin π-bond, the C$_2$=C$_3$ olefin remaining uncoordinated. This complex has been the subject of a previous communication.[8] In order to establish whether (1) is produced by thermal decomposition of (4) or by the attack of the bicyclic diene C_8H_{10} on this complex, a benzene solution of H$_2$(C_8H_8)Ru$_3$(CO)$_9$ was refluxed for 25 h; no conversion into (2—4, 6-η-C_8H_{10})Ru(CO)$_3$ was observed. However when the 3-^{2}H deuteriated diene C_8H_9D was added to this refluxing solution, (1) and (2) were formed. The ^{1}H n.m.r. spectrum of complex (1) so obtained shows incorporation of deuterium in the C-3 allylic position, indicating that the diene which participates in the formation of (1) is the incoming diene. The production of the complex (2—4,6-η-C_8H_9D)Ru(CO)$_3$ from H$_2$(C_8H_8)Ru$_3$(CO)$_9$ may be visualized in three different ways: (1) exchange of the organo-group in (4) followed by attack of another diene molecule on this complex to release (C_8H_9D)Ru(CO)$_3$; (2) (C_8H_{10})-Ru(CO)$_3$ is released from (4) under the attack of a C_8H_9D molecule, and then the diene is exchanged to

give (C_8H_9D)Ru(CO)$_3$; (3) C_8H_9D becomes attached to the metal atom of a Ru(CO)$_3$ unit which is released from complex (4) to form a (C_8H_9D)Ru(CO)$_3$ molecule. The low yield of complex (1) (15·3% based on Ru), from the reaction of Ru$_3$(CO)$_{12}$ with the bicyclic diene C_8H_{10}, is consistent with any of these mechanisms,

[7] A. Eisenstadt and S. Winstein, *Tetrahedron Letters*, 1970, **52**, 4603.

[8] A. J. P. Domingos, B. F. G. Johnson, and J. Lewis, *J. Organometallic Chem.*, 1972, **36**, C43.
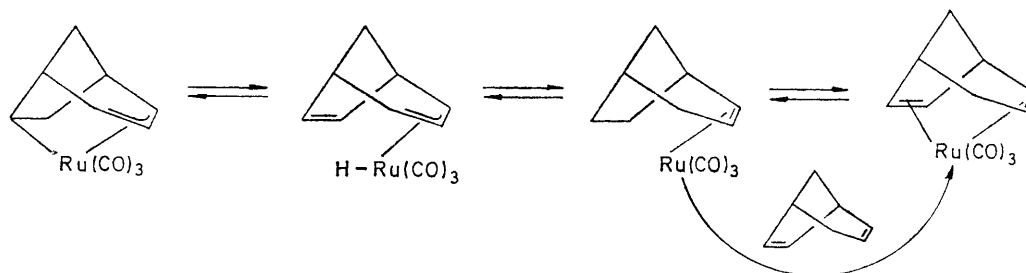
according to which, a maximum of 33·3% is anticipated. Although we were not able to determine the mechanism solely responsible, the feasibility of the second was easily demonstrated. The ^{1}H n.m.r. spectrum of the complex (1) isolated from a benzene solution of bicyclo-[3.2.1]octa-1,6-diene and the exo-7-^{2}H derivative of this complex (refluxed for 10 h) showed that this deuterium had been lost, indicating the complete exchange of the diene.

Infrared monitoring of refluxing solutions of the bicyclic diolefin C_8H_{10} and the exo-7-^{2}H deuteriated (1) indicated that three new bands appeared at 2047,

(1)   benzene
                                       (reflux)
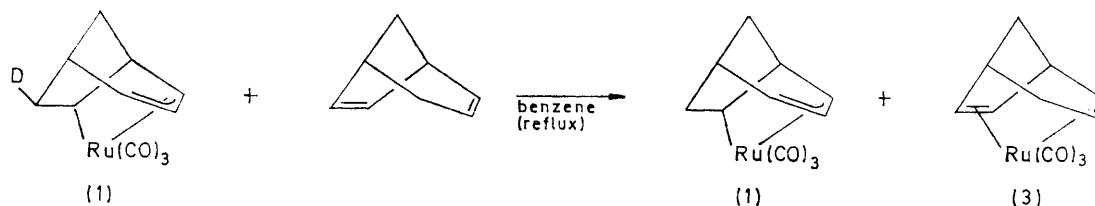
1985, and 1968 cm^{-1}, and that the intensities of these bands depend on the concentration of the diolefin. We were unable to isolate the new species formed in this reaction but since the three new infrared bands are similar to those of $(1,5-C_8H_{12})Ru(CO)_3$,[2] the new species is presumed to be (2,3,6,7-η-bicyclo[3.2.1]octa-diene)tricarbonylruthenium, complex (3). In support of this suggestion, the yield of the cationic complex $[(2\text{—}4,6,7\text{-}\eta\text{-}C_8H_9)Ru(CO)_3]^+$, is increased from 53 to 68% when changing to a mixture of complexes (1) and (3) (3 : 1, infrared estimate).

The mechanism represented in the following scheme accounts for the isomerization of complex (1) to (3), the

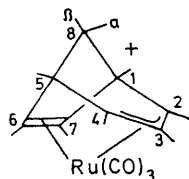does not bring about the dimerization of the ligand and that for this dimerization to occur it is necessary to have $H_2(C_8H_8)Ru_3(CO)_9$ present.

A solution of triphenylmethyl tetrafluoroborate in dichloromethane reacts readily at room temperature with an equimolar amount of (2—4,6-η-bicyclo[3.2.1.]-octadiene)tricarbonylruthenium in the same solvent. Addition of diethyl ether precipitates stable, white crystals which are recrystallized first from dichloromethane and then from liquid sulphur dioxide. The infrared spectrum in dichloromethane, exhibiting a sharp band at 2125 cm^{-1} and a broad band at 2060 cm^{-1}

(1)   (3)

with a shoulder at 2080 cm^{-1}, is consistent with the presence of a $Ru(CO)_3$ group in the molecule. These C–O stretching vibrations are similar to those of the $Ru(CO)_3$ unit in the cationic complex $[(1\text{—}3,5,6\text{-}\eta\text{-}C_8H_{11})Ru(CO)_3]^+$. The compound had an analysis consistent with the empirical formula $C_{11}H_9O_3RuBF_4$ and is formulated as $[(2\text{—}4,6,7\text{-}\eta\text{-}C_8H_9)Ru(CO)_3]BF_4$, (5), on the basis of its 100 MHz ^{1}H n.m.r. spectrum which in liquid sulphur dioxide (Figure 3) exhibits the following features: a triplet at τ 4·96 which may be assigned to the central allylic proton 3-H; a complex multiplet centralised at τ 5·55 due to overlapping 'outer' allylic protons and olefinic protons, 2-H,

ligand exchange, and the dependence of the ratio $[(3)]/([1])]$ on the concentration of the bicyclic ligand in solution. Further confirmation of this hydride migration was obtained by refluxing a benzene solution of the exo-7-^{2}H deuteriated (1). Although substantial decomposition occurred, the ^{1}H n.m.r. spectrum of the mixture of the complexes (2—4,6-η-C_8H_9D)Ru(CO)$_3$ isolated differs from the spectrum of the original complex in that the absorption at τ 8·17 (H$_7$) integrates to ca. 1·5 protons and the low field side of the τ 9·1—9·4 multiplet (6-H) besides being less intense, exhibits more coupling. This is consistent with the production of the 6-^{2}H derivative of complex (1).

In neither this last reaction nor in the previous ligand exchange reactions was the formation of $(C_{16}H_{20})$-Ru(CO)$_3$ observed. It appears that complex (1)

4-H, 6-H, and 7-H; a multiplet at τ 6·60 arising from the two bridge-head protons 1-H and 5-H; a doublet of triplets at τ 8·32 due to the bridge proton 8β-H; and a doublet at τ 8·97 assigned to the bridge proton 8α-H. The assignment of the spectrum is based on double-irradiation experiments: the 3-H triplet changed to a sharp singlet on irradiation at the τ 5·45—5·65 multiplet; the τ 5·45—5·65 multiplet (2-H, 4-H, 6-H, 7-H) was modified by irradiation at 3-H or at 1-H + 5-H; the τ 6·60 absorption (1-H + 5-H) was a doublet on irradiation at the τ 5·45—5·65 multiplet and a simplified multiplet on irradiation at 8β-H; the 8β-H doublet of triplets became sharper on irradiation at the τ 5·45—5·65 multiplet and gave a doublet on irradiation at 1-H + 5-H; the 8α-H doublet changed to a sharp singlet on irradiation at 8β-H. The τ 8·32 doublet

of triplets was assigned as 8β-H, and not as 8α-H, based on the discussion of the dependence of coupling constants on the dihedral angles of the planes defined by H(1)[H(5)]–C–C–H(8β)[H(8α)], estimated from a

1-H, 5-H	τ 6·60	$J_{12} = J_{45} = 6$ Hz
2-H, 4-H	τ 5·59	$J_{23} = J_{34} = 6·0$ Hz
3-H	τ 4·96	$J_{17} = J_{56} = 2·8$ Hz
6-H, 7-H	τ 5·47	$J_{16} = J_{57} = 1·8$ Hz
8α-H	τ 8·97	$J_{1\beta} = J_{5\beta} = 4·2$ Hz
8β-H	τ 8·32	$J_{\alpha\beta} = 11$ Hz
		$\Delta\nu = 65$ Hz

FIGURE 3   [1]H N.m.r. data for [(2—4,6,7-η-C$_8$H$_9$)-Ru(CO)$_3$]$^+$ in liquid SO$_2$

molecular model of the complex. The 220 MHz spectrum resolved the τ 5·45—5·65 multiplet in a triplet at τ 5·59 and a doublet of doublets at τ 5·47. Decoupling experiments at 220 MHz allowed the assignment of the τ 5·59 triplet to 2-H and 4-H and of the τ 5·47 doublet of doublets to the olefinic protons 5-H and 7-H: the 6-H and 7-H absorption gave a sharp singlet on irradiation at 1-H + 5-H; the 2-H + 4-H triplet gave a doublet on irradiation at 1-H + 5-H. Apart from small changes in the chemical shifts and coupling constants of corresponding protons, the n.m.r. spectrum of (5) is in good agreement with the spectra of the cationic bicyclo[3.2.1]octadienyl-,[9] bicyclo[3.2.2]-nonadienyl-,[7] and 6,7-benzobicyclo[3.2.2]nonadienyl-complexes [10] of Fe(CO)$_3$.

Reduction of [(2—4,6,7-η-C$_8$H$_9$)Ru(CO)$_3$]$^+$ with lithium borodeuteride in deuterium oxide gave the *exo*-7-^{2}H derivative of complex (1), (2—4,6-η-C$_8$H$_9$D)Ru(CO)$_3$, as the sole product.

EXPERIMENTAL

Dodecacarbonyltriruthenium was prepared from ruthenium trichloride and carbon monoxide by the method of Bruce and Stone (10 atm CO; Zn) [11] and recrystallized twice from benzene. Bicyclo[3.2.1]octa-2,6-diene and 3-bromo-bicyclo[3.2.1]octa-2,6-diene were prepared as described in the literature.[6] Triphenylmethyl tetrafluoroborate was prepared from triphenylmethanol and tetrafluoroboric acid in propionic anhydride.[12] Reactions and purifications were done under nitrogen.

[3-[2]H$_1$]*Bicyclo*[3.2.1]*octa*-2,6-*diene*.—A solution of 3-bromobicyclo[3.2.1]octa-2,6-diene (18·5 g, 0·10 mol) and 1,2-dibromoethane (18·6 g, 0·10 mol) in tetrahydrofuran (100 ml) was added dropwise during 12 h to a flask with magnesium (9·72 g, 0·4 mol) in the same solvent (100 ml) under reflux and with stirring. Another solution of C$_2$H$_4$Br$_2$ (2·3 g, 0·025 mol) in tetrahydrofuran (12 ml) was then added and reflux and stirring were continued for a further 2 h. All the tetrahydrofuran used had been distilled from calcium hydride. The mixture was hydro-

[9] T. N. Margulis, L. Schiff, and M. Rosenblum, *J. Amer. Chem. Soc.*, 1965, **87**, 3269.
[10] A. Eisenstadt, *J. Organometallic Chem.*, 1972, **28**, C32.

lysed with D$_2$O (60 ml) and some drops of D$_2$SO$_4$, and then filtered through dry glass wool and extracted with diethyl ether after the addition of more D$_2$SO$_4$ (10 ml). The extracts were dried (MgSO$_4$) and the solvents distilled under reduced pressure (12 mmHg) through a 0 °C cooled column equipped with a cold finger (—10 °C) on the top. The diene was distilled under reduced pressure (~20 °C; 12 mmHg) and dried (Ca$_2$SO$_4$). Bulb-to-bulb distillation (0·005 mmHg) gave the [3-[2]H$_1$]bicyclo[3.2.1]octa-2,6-diene (6·7 g, 0·063 mol) in 63% yield. Its [1]H n.m.r. spectrum indicated that 80% incorporation of deuterium at the C-3 olefinic carbon had occurred.

(*2—4,6-η-Bicyclo*[3.2.1]*octadiene*)*tricarbonylruthenium and* (C$_{16}$H$_{20}$)*Tricarbonylruthenium*.—Successive small volumes (0·15 ml) of bicyclo[3.2.1]octa-2,6-diene (total: 3·67 g, 35 mmol) were added to a refluxing solution of Ru$_3$(CO)$_{12}$ (640 mg, 1 mmol) in benzene (100 ml), until the infrared monitoring of the reaction indicated that all the H$_2$(C$_8$H$_8$)-Ru$_3$(CO)$_9$ intermediate formed, had been consumed (*ca.* 50 h). The solvent and the excess of diene were removed, and the residue was treated with pentane; the pentane extract was then concentrated. Successive chromatographies (seven) with pentane on silica columns, isolated two bands absorbing at respectively 2067, 1999 cm^{-1} and 2067, 1999, 1994 cm^{-1}. Monitoring of these column chromatographies, by running infrared spectra of the eluates as they passed through an infrared cell connected to the outlet of the column, was essential to separate the two bands. The first band gave, on evaporation of the solvent, a colourless oil which on distillation (room temperature 1 mmHg) to a cold finger at —20 °C yielded (2—4,6-η-C$_8$H$_{10}$)Ru(CO)$_3$ (134 mg, 46% based on Ru$_3$) as white crystals melting at *ca.* —10 °C (Found: C, 45·5; H, 3·45. Calc.: C, 45·36; H, 3·46). The second band gave (C$_{16}$H$_{20}$)Ru(CO)$_3$ (62 mg, 15·6% based on Ru$_3$) as yellow crystals (Found: C, 58·2; H, 4·9. Calc.: C, 57·42; H, 5·07).

(*2—4,6,7-η-Bicyclo*[3.2.1]*octadienyl*)*tricarbonylruthenium Tetrafluoroborate*.—Dichloromethane solutions of (2—4,6-η-C$_8$H$_{10}$)Ru(CO)$_3$ (134 mg, 0·44 mmol/in 0·2 ml) and Ph$_3$CBF$_4$ (175 mg, 0·53 mmol/in 2 ml) were mixed and shaken for 30 min. Addition of diethyl ether formed a pale yellow precipitate which was left in the air in order to hydrolyse the unchanged Ph$_3$CBF$_4$. Recrystallizations, from dichloromethane with addition of diethyl ether, and from liquid sulphur dioxide, yielded [(2—4,6,7-η-C$_8$H$_9$)Ru(CO)$_3$]-BF$_4$ (94 mg, 53%) as air stable white crystals (Found: C, 35·2; H, 2·55. Calc.: C, 35·04; H, 2·41).

Deuteride Attack on [(2—4,6,7-η-C$_8$H$_9$)Ru(CO)$_3$]BF$_4$.—Deuterium oxide solutions of LiBD$_4$ (103 mg, 4 mmol) and [(2—6,7-η-C$_8$H$_9$)Ru(CO)$_3$]BF$_4$ (94 mg, 0·25 mmol) were mixed at 0 °C and stirred for 15 min. The mixture was extracted with diethyl ether and the extracts dried (MgSO$_4$). The brownish oil obtained was chromatographed with pentane on a silica column, and distilled (room temperature, 1 mmHg) onto a cold finger at —20 °C, to yield [3-^{2}H]-(2—6-η-C$_8$H$_9$D)Ru(CO)$_3$ (46 mg, 65%

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