Reactions of Co-ordinated Ligands. Part 34.[1] Synthesis, Structure, and Reactivity of Cationic Dieneruthenium Complexes; Crystal Structures of $[Ru(\eta^4\text{-}C_6H_8)(CO)(\eta\text{-}C_5H_5)][BF_4]$ and $[Ru(\eta^3\text{-}C_6H_9)(CO)(\eta\text{-}C_5H_5)]$†

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Ultraviolet irradiation of a solution of $[Ru(NCMe)(CO)_2(\eta\text{-}C_5H_5)][BF_4]$ in MeCN affords $[Ru(NCMe)_2(CO)(\eta\text{-}C_5H_5)][BF_4]$ (**1**) in high yield. The acetonitrile ligands in complex (**1**) are substitution labile and reaction with buta-1,3-diene, isoprene, 1,4-diphenylbuta-1,3-diene, and cyclohexa-1,3-diene gives the complexes $[Ru(\eta^4\text{-}1,3\text{-diene})(CO)(\eta\text{-}C_5H_5)][BF_4]$. An *X*-ray crystallographic study on the cyclohexa-1,3-diene cation established that the molecule adopts an *exo* configuration, the C_6 ring showing substantial folding. Whereas *trans*-penta-1,3-diene reacts with complex (**1**) to form an analogous complex, *cis*-penta-1,3-diene affords an isomeric mixture of *exo* and *endo* isomers of both the *cis*- and *trans*-penta-1,3-diene complexes. This is discussed in terms of a hydrogen-shift process involving a $Ru^{II} \longrightarrow Ru^{IV}$ redox reaction. Cyclo-octa-1,3-diene does not react with complex (**1**), however, both cyclo-octa-1,5-diene and cyclo-octatetraene react to form $[Ru(\eta^4\text{-}1,5\text{-}C_8H_{12})(CO)(\eta\text{-}C_5H_5)][BF_4]$ and $[Ru(\eta^4\text{-}C_8H_8)(CO)(\eta\text{-}C_5H_5)][BF_4]$, u.v. irradiation of the latter complex affording $[Ru(\eta^6\text{-}C_8H_8)(\eta\text{-}C_5H_5)][BF_4]$. This is possibly related to a close relationship between the fragments $Ru(CO)(\eta\text{-}C_5H_5)^+$ and $Cr(CO)_4$. Reaction of the buta-1,3-diene and isoprene cations with $Li[CuPh_2]$ and $Na[BH_3(CN)]$ respectively affords η^3-allyl complexes. An *X*-ray crystallographic study on the η^3-cyclohexenyl complex, $[Ru(\eta^3\text{-}C_6H_9)(CO)(\eta\text{-}C_5H_5)]$, obtained on reaction of the cyclohexa-1,3-diene cation with $Na[BH_3(CN)]$ showed that the C_6 ring adopts a boat conformation. Consideration of this observation along with ^1H n.m.r. data is used to show that nucleophilic reagents attack the opposite face of the C_6 ring to which the ruthenium is bonded. The cyclo-octa-1,5-diene complex reacts with $Na[BH_3(CN)]$ to form a 1,4,5-η^3-C_8H_{13} complex, which does not isomerise to a 1,2,3-η^3-bonded species.

Cationic η^4-1,3-diene complexes of molybdenum have recently been the focus of some attention, principally with a view to their utilisation in the synthesis of naturally occurring organic molecules.[2-4] In this respect the binding of cyclohexa-1,3-diene derivatives to molybdenum has been of particular interest, since it allows the regio- and stereo-selective introduction of carbon substituents, as demonstrated by Pearson's[4] stereocontrolled lactone synthesis. In comparison the chemistry of the related cations $[Ru(\eta^4\text{-diene})(CO)(\eta\text{-}C_5H_5)][BF_4]$ has not been explored, although a number of the corresponding iron complexes[5] have been synthesised. In this paper we describe the synthesis and structural characterisation of a range of cationic ruthenium diene complexes, and the stereochemistry of their reaction with nucleophilic reagents.

Results and Discussion

Recently Steinmetz and Johnson[6] reported on the reactions of the salt $[Ru(NCMe)_2(CO)(\eta\text{-}C_5H_5)][BF_4]$ (**1**) with amines. We have independently prepared (**1**) in high yield by u.v. irradiation of an acetonitrile solution of $[Ru(NCMe)(CO)_2(\eta\text{-}C_5H_5)][BF_4]$, the latter being formed by the cleavage of $[\{Ru(CO)_2(\eta\text{-}C_5H_5)\}_2]$ with $AgBF_4$ in a CH_2Cl_2–MeCN solution. The acetonitrile ligands present in complex (**1**) are substitution labile in solution at room temperature as illustrated by the observation that a ^1H n.m.r. spectrum of (**1**) in CD_3CN showed complete replacement of the co-ordinated MeCN by CD_3CN in 2 d. Buta-1,3-diene, isoprene, 1,4-diphenylbuta-1,3-diene, and cyclohexa-1,3-diene also reacted with (**1**) in CH_2Cl_2 solution to form good yields of the 1,3-diene cations (**2**)—(**5**), which were isolated as air-stable white crystalline materials and characterised by analysis, i.r., ^1H and $^{13}C\text{-}\{^1H\}$ n.m.r. spectroscopy. The n.m.r. spectra were temperature invariant and showed signals corresponding to the presence of only one isomer.

In view of the potential importance of the cyclohexa-1,3-diene cation (**5**), a single-crystal *X*-ray diffraction study was undertaken. The crystal structure of (**5**) consists of isolated cations and anions showing no short contacts. The molecular geometry of the cation is illustrated in Figure 1. Table 1 lists

Table 1. Atomic co-ordinates (× 10^4) for complex (**5**)

Atom	*x*	*y*	*z*
Ru	2 927(1)	2 500	4 425(1)
C(12)	4 590(6)	2 500	4 195(5)
O	5 563(5)	2 500	3 980(4)
C(7)	2 764(8)	2 500	2 702(6)
C(2)	3 471(5)	1 074(5)	5 840(4)
C(1)	2 384(4)	1 739(6)	5 990(3)
C(8)	2 162(6)	1 271(9)	3 091(5)
C(3)	4 565(4)	1 667(6)	6 353(4)
C(9)	1 238(5)	1 757(7)	3 700(4)
B	3 544(8)	2 500	9 494(7)
F(1)	3 481(7)	1 396(6)	10 204(5)
F(2)	2 654(5)	2 500	8 807(7)
F(3)	4 507(5)	2 500	9 046(5)

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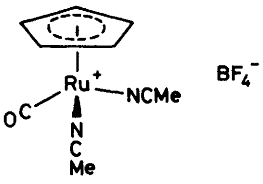
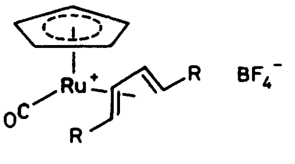
† Carbonyl(η-cyclohexa-1,3-diene)(η-cyclopentadienyl)ruthenium(II) tetrafluoroborate and carbonyl(1—3-η-cyclohexenyl)(η-cyclopentadienyl)ruthenium(II).

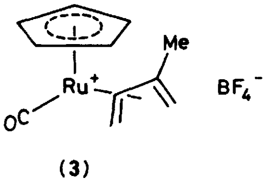
Supplementary data available (No. SUP 56281, 8 pp.): thermal parameters, H-atom co-ordinates. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1985, Issue 1, pp. xvii—xix. Structure factors are available from the editorial office.



(1)



(2; $R^1 = R^2 = H$)
(4; $R^1 = R^2 = Ph$)



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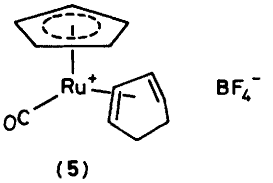
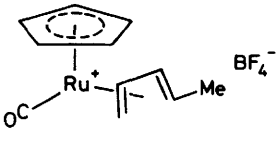
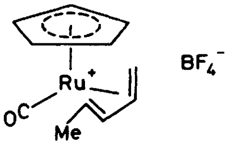


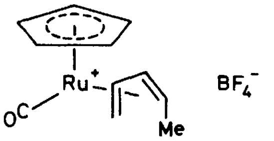
(5)



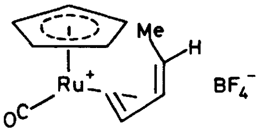
(6a)



(6b)



(7a)



(7b)

the non-hydrogen atomic positional parameters. Table 2 gives the derived interatomic distances and interbond angles.

The cation shows crystallographic mirror symmetry with the ruthenium atom being co-ordinated by an η^5-cyclopentadienyl ligand [Ru–C 2.168(7)*—2.216(6) Å], a linear carbonyl ligand [Ru–C(12) 1.892(7) Å, Ru–C(12)–O 174.9(6)°], and an η^4-cyclohexa-1,3-diene ligand [with no carbon atoms on the mirror plane, Ru–C(1) (inner) 2.175(4) and Ru–C(2) (outer) 2.298(5) Å]. The cyclohexa-1,3-diene is in the *exo* orientation relative to the cyclopentadienyl ring and shows C–C lengths within the diene fragment of 1.383(7) Å [C(1)–C(2)] and 1.415(11) Å [C(1)–C(1′)]. The C_6 ring is markedly folded such that the angle between the C(2),C(1),C(1′),C(2′) and C(2),C(3),C(3′),C(2′) planes is 36.4°. In the neutral complex $[Ru(CO)_3(\eta^4\text{-}C_{16}H_{16})]$[7] the related interplanar angle is 39°. Other reported cyclohexa-1,3-diene complexes include $[Mo(\eta^4\text{-}1,3\text{-}C_6H_8)(dppe)(\eta\text{-}C_5H_5)][PF_6]\cdot SO_2$ (dppe = $Ph_2PCH_2CH_2PPh_2$), in which the dihedral angle is 44.5°,[8] and a series of substituted tricarbonyliron complexes where the angle varies from 36.3 to 39.9°.[9]

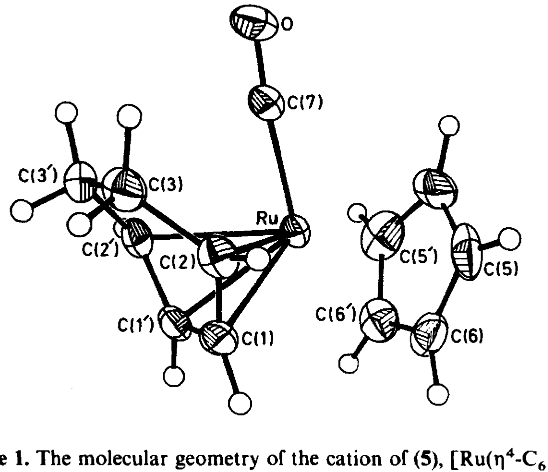


Figure 1. The molecular geometry of the cation of (5), $[Ru(\eta^4\text{-}C_6H_8)(CO)(\eta\text{-}C_5H_5)]^+$, showing the atomic labelling scheme used

When *trans*-penta-1,3-diene (C_5H_8) was treated with complex (1) no isomerisation occurred and the *exo* complex $[Ru(\eta^4\text{-}\mathit{trans}\text{-}C_5H_8)(CO)(\eta\text{-}C_5H_5)][BF_4]$ (**6a**) was obtained as white crystals. However, the corresponding reaction of *cis*-penta-1,3-diene afforded (by ^1H n.m.r.) an isomeric mixture (39:28:11:4) of *exo* and *endo* isomers of both $[Ru(\eta^4\text{-}\mathit{cis}\text{-}C_5H_8)(CO)(\eta\text{-}C_5H_5)][BF_4]$ (**7a**) and (**7b**) and $[Ru(\eta^4\text{-}\mathit{trans}\text{-}C_5H_8)(CO)(\eta\text{-}C_5H_5)][BF_4]$ (**6a**) and (**6b**) (Scheme 1). Additionally it was observed that when the reaction was complete the relative proportions of these isomers were not affected by variation in temperature, and examination of the unreacted penta-1,3-diene from the reaction mixture showed it to contain only the *cis* isomer.

In the case of the related molybdenum system $[Mo(\eta^4\text{-}C_5H_8)(CO)_2(\eta\text{-}C_5H_5)]^+$ [ref. 10(*a*)] it was shown by examination of the temperature-dependent ^1H n.m.r. spectrum that *exo*- and *endo*- and *cis*-/*trans*-penta-1,3-dienes are present in solution in equilibrium. The equilibrium process was explained by postulating that an 'envelope flip' motion was occurring within a solvent-stabilised metallocyclopent-3-ene intermediate. Clearly since the relative proportions of (**6a**)/(**6b**) and (**7a**)/(**7b**) were not affected by variation in temperature, such a mechanism could not be operating with the ruthenium penta-1,3-diene cations, and it is more likely that a metal-assisted hydrogen-shift process is involved.

If we consider first the reaction with *cis*-penta-1,3-diene (Scheme 1) a likely initial step is dissociative loss of MeCN from complex (1) to form a 16-electron species, which is captured by the 1,3-diene to give an η^2-bonded species where the unsubstituted olefinic bond is co-ordinated to the ruthenium. Dissociative loss of the second MeCN then creates a vacant co-ordination site, which can be satisfied either by irreversible formation of an η^4-bonded 1,3-diene complex, or by transfer of the ruthenium fragment onto the methyl-substituted double bond and generation of an agostic[11] interaction between the ruthenium and one of the three methyl-group hydrogens. This latter interaction on further development leads to complete transfer of the interacting hydrogen from carbon to ruthenium, *i.e.* a formal oxidative $Ru^{II} \longrightarrow Ru^{IV}$ reaction. In order to achieve *cis* to *trans* isomerisation of the penta-1,3-diene it is then necessary for rotation to occur about a C–C bond, slippage[12] of the ruthenium fragment along the five-carbon chain, followed by rotation about a Ru–C bond, thus positioning the Ru–H bond *cis* to the η^3-allyl so that hydrogen transfer can regenerate a penta-1,3-diene ligand. This sequence of reactions is illustrated in Scheme 1, where only one rotamer of the initially formed η^2-bonded 1,3-diene species is shown. The

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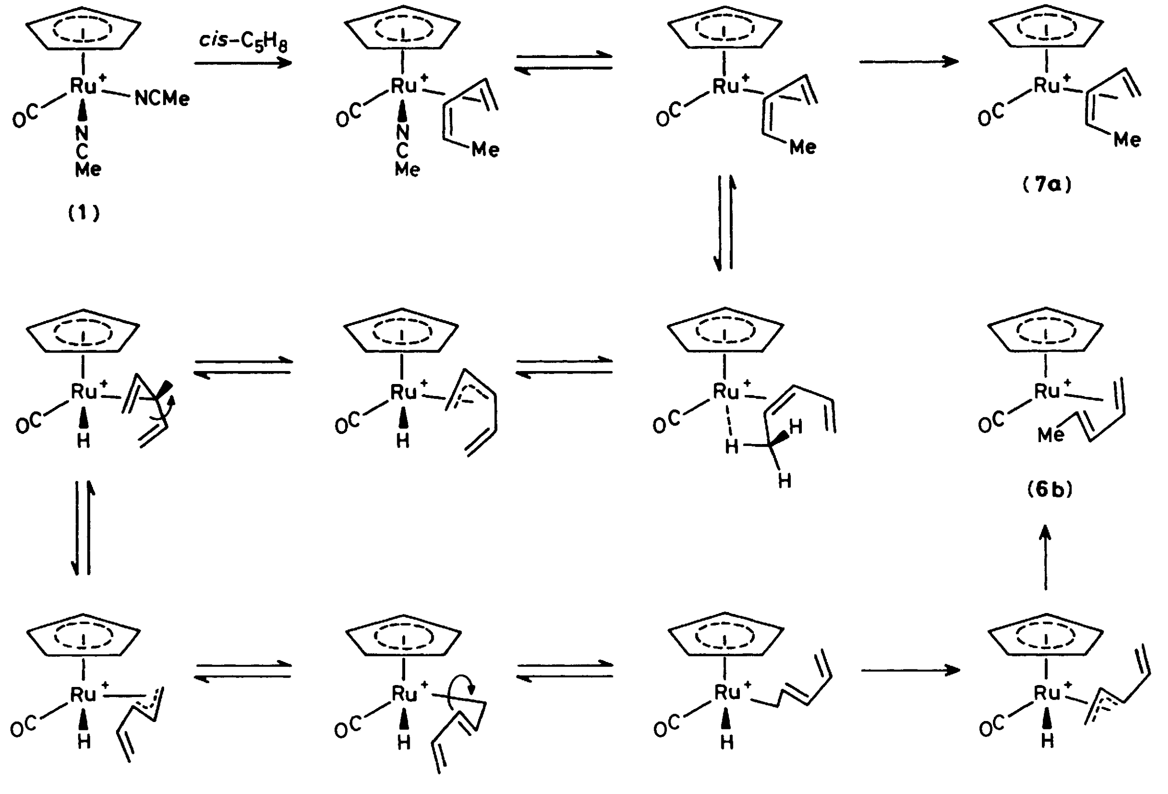
* Estimated standard deviations in the least significant digit are given in parentheses here and throughout this paper.

Table 2. Bond lengths (Å) and angles (°) for complex (**5**)

Ru–C(12)	1.892(7)	C(12)–O	1.127(9)	C(9)–C(9′)	1.382(12)	C(1)–C(1′)	1.415(11)
Ru–C(2)	2.298(5)	C(7)–C(8′)	1.415(9)	C(7)–C(8)	1.415(9)	C(3)–H(3)	1.011(57)
Ru–C(8)	2.201(7)	C(2)–C(3)	1.494(7)	C(2)–C(1)	1.383(7)	C(3)–C(3′)	1.548(11)
Ru–C(7)	2.168(7)	C(1)–H(1)	0.932(62)	C(2)–H(2)	0.848(59)	B–F(1)	1.360(8)
Ru–C(1)	2.175(4)	C(8)–C(9)	1.367(9)	B–F(2)	1.321(11)	B–F(3)	1.220(11)
Ru–C(9)	2.216(6)	C(3)–H(4)	0.901(51)				

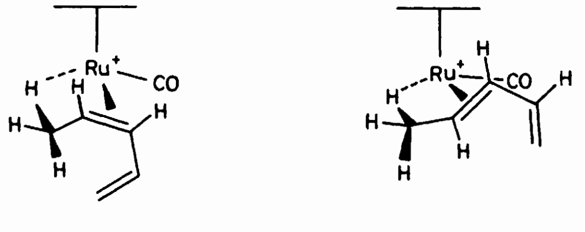
C(12)–Ru–C(7)	86.1(3)	C(12)–Ru–C(2)	81.6(2)	C(1)–Ru–C(9′)	103.3(2)	C(8)–Ru–C(9′)	61.0(2)
C(7)–Ru–C(2)	142.4(1)	C(12)–Ru–C(1)	114.5(2)	C(9)–Ru–C(9′)	36.3(3)	Ru–C(12)–O	174.9(6)
C(7)–Ru–C(1)	151.2(2)	C(2)–Ru–C(1)	35.9(2)	Ru–C(7)–C(8)	72.3(4)	Ru–C(7)–C(8′)	72.4(4)
C(12)–Ru–C(8)	105.7(2)	C(7)–Ru–C(8)	37.8(2)	C(8)–C(7)–C(8′)	107.8(8)	Ru–C(2)–C(1)	67.2(3)
C(2)–Ru–C(8)	113.0(2)	C(1)–Ru–C(8)	114.0(2)	Ru–C(2)–C(3)	109.8(3)	C(1)–C(2)–C(3)	120.3(4)
C(12)–Ru–C(9)	141.7(2)	C(7)–Ru–C(9)	61.2(3)	Ru–C(2)–H(2)	115.2(32)	C(1)–C(2)–H(2)	117.6(37)
C(2)–Ru–C(9)	111.4(2)	C(1)–Ru–C(9)	91.6(2)	C(3)–C(2)–H(2)	116.3(36)	Ru–C(1)–C(2)	76.9(3)
C(8)–Ru–C(9)	36.1(2)	C(12)–Ru–C(2′)	81.6(2)	Ru–C(1)–H(1)	125.2(37)	C(2)–C(1)–H(1)	130.8(37)
C(7)–Ru–C(2′)	142.4(1)	C(2)–Ru–C(2′)	70.5(2)	Ru–C(1)–C(1′)	71.0(1)	C(2)–C(1)–C(1′)	116.6(3)
C(1)–Ru–C(2′)	64.2(2)	C(8)–Ru–C(2′)	172.1(2)	H(1)–C(1)–C(1′)	112.4(37)	Ru–C(8)–C(7)	69.9(4)
C(9)–Ru–C(2′)	136.4(2)	C(12)–Ru–C(1′)	114.5(2)	Ru–C(8)–C(9)	72.6(4)	C(7)–C(8)–C(9)	106.8(6)
C(7)–Ru–C(1′)	151.1(2)	C(2)–Ru–C(1′)	64.2(2)	C(2)–C(3)–H(3)	118.1(32)	C(2)–C(3)–H(4)	101.8(31)
C(1)–Ru–C(1′)	38.0(3)	C(8)–Ru–C(1′)	138.2(2)	H(3)–C(3)–H(4)	104.0(43)	C(2)–C(3)–C(3′)	111.6(3)
C(9)–Ru–C(1′)	103.3(2)	C(12)–Ru–C(8′)	105.7(2)	H(3)–C(3)–C(3′)	109.7(31)	H(4)–C(3)–C(3′)	110.9(31)
C(7)–Ru–C(8′)	37.8(2)	C(2)–Ru–C(8′)	172.1(2)	Ru–C(9)–C(8)	71.4(4)	Ru–C(9)–C(9′)	71.8(2)
C(1)–Ru–C(8′)	138.2(2)	C(8)–Ru–C(8′)	62.6(4)	C(8)–C(9)–C(9′)	109.3(4)	F(1)–B–F(2)	112.8(6)
C(9)–Ru–C(8′)	61.0(2)	C(12)–Ru–C(9′)	141.7(2)	F(1)–B–F(3)	110.4(6)	F(2)–B–F(3)	111.8(8)
C(7)–Ru–C(9′)	61.2(3)	C(2)–Ru–C(9′)	136.4(2)	F(1)–B–F(1′)	97.9(7)		



Scheme 1.

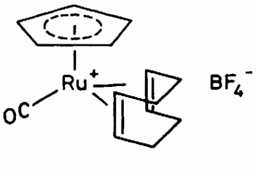
other rotamer obtained by rotation about an axis through the metal and perpendicular to the C–C bond would by a similar process (due to non-bonding interactions probably less favoured) generate the *endo-cis* isomer (**6b**) and *exo-trans* isomer (**7a**).

As was previously mentioned, *cis* to *trans* isomerisation does not occur on reaction of *trans*-penta-1,3-diene with complex (**1**). This can be explained by comparing the two isomeric species (**A**) and (**B**) shown in Scheme 2, which are formed when CHRu interactions develop with η^2-bonded *cis*- and *trans*-penta-1,3-diene respectively. In the case of (**B**) an unfavourable non-bonding interaction with the co-ordinated CO could occur, and thus simple collapse to an η^4-bonded *trans*-penta-1,3-diene cation would be the preferred pathway.



(A) (B)

Scheme 2.



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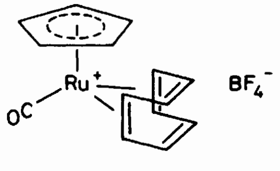

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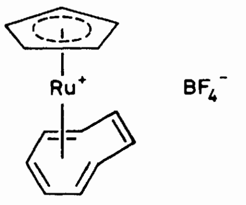

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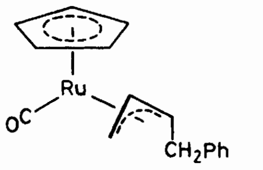

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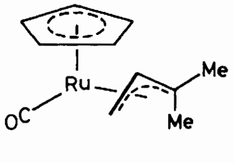

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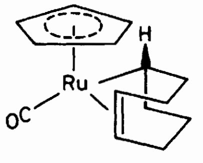

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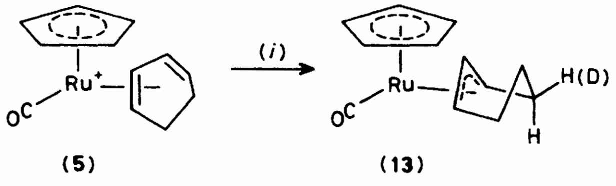


(5) (13)

Scheme 3. (*i*) Na[BH$_3$(CN)], thf

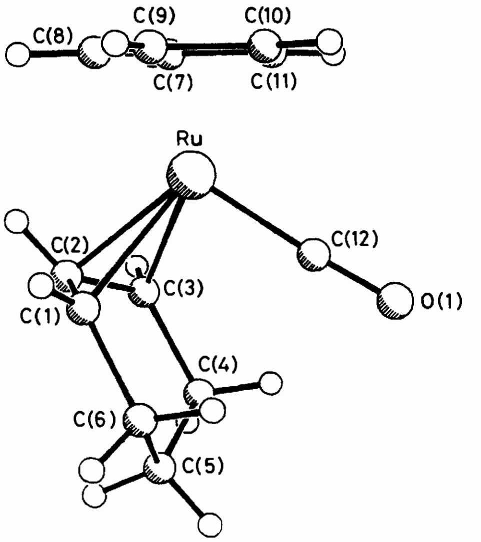


Figure 2. The molecular geometry of (**13**), [Ru(η^3-C$_6$H$_9$)(CO)(η-C$_5$H$_5$)], showing the atomic labelling scheme used

Although the reversible formation of an allylhydride is generally accepted[13] as a step in the isomerisation of olefins by a variety of metal species, the possible involvement of a Ru^{II}–Ru^{IV} redox process is unusual. There is, however, precedent in that a key step in the use of [Ru(η^4-C$_6$Me$_6$)(η^6-C$_6$Me$_6$)] as a homogeneous catalyst for the hydrogenation of aromatics is thought[14] to involve the reversible addition of H$_2$ to a ruthenium(II) η^3-benzyl hydride intermediate. Oxidative addition of halogens to [RuCl(PMe$_3$)$_2$(η-C$_5$H$_5$)][15] or [RuBr(CO)$_2$(η-C$_5$Me$_4$Et)][16] has also been shown to give ruthenium(IV) species. Recently,[17] the synthesis and structural characterisation of the rhodium(V) complex [RhH$_2$(SiEt$_3$)$_2$(η-C$_5$Me$_5$)] has led to the important suggestion that high oxidation states in the organometallic chemistry of the platinum metals might be more important than hitherto recognised.

Additional insight into the co-ordinating ability of the Ru(CO)(η-C$_5$H$_5$)$^+$ fragment was obtained on examining the reactions of complex (**1**) with cyclo-octadienes and cyclo-octatetraene. Whilst cyclo-octa-1,5-diene reacts readily with the bis(acetonitrile) cation to yield the η^4-1,5-diene complex (**8**), cyclo-octa-1,3-diene did not react and was not isomerised to the 1,5-diene. Furthermore, cyclo-octatetraene reacted slowly with (**1**) to give [Ru(η^4-C$_8$H$_8$)(CO)(η-C$_5$H$_5$)][BF$_4$] (**9**), where the η^4-C$_8$H$_8$ is stereochemically rigid. These results are attributable to the fact that the d^6 RuL(η-C$_5$H$_5$)$^+$ fragment is isolobal with the Cr(CO)$_4$ fragment[18,19] which shows a slight preference towards bonding with unconjugated dienes, for which the highest occupied and lowest unoccupied molecular orbitals (h.o.m.o. and l.u.m.o.) are well separated in energy and match fairly closely those of the d^6 fragment.

As anticipated, u.v. irradiation of a CH$_2$Cl$_2$ solution of complex (**9**) led to the evolution of carbon monoxide, and the formation of a sandwich complex [Ru(η^6-C$_8$H$_8$)(η-C$_5$H$_5$)][BF$_4$] (**10**), the high stability of which is in accordance with that observed for the related complexes [Ru(η^6-C$_6$Ph$_4$R′R″)(η-C$_5$H$_5$)][BF$_4$] and [Ru(η^2-C$_2$H$_4$)$_3$(η-C$_5$H$_5$)][BF$_4$].

The reactions of the complexes (**2**), (**3**), (**5**), and (**9**) with nucleophilic reagents were next examined. Addition of lithium diphenylcuprate to the buta-1,3-diene complex (**2**) in tetrahydrofuran (thf) afforded the η^3-allyl complex [Ru(η^3-CH$_2$$\cdots$CH$\cdots$CHCH$_2$Ph)(CO)($\eta$-C$_5H_5$)] (**11**). Comparison of the ^{1}H n.m.r. spectrum with those reported[10] for related complexes enabled the η^3-allyl complex to be assigned to an *exo* configuration, the benzyl group occupying an *anti* configuration. The isoprene cation (**3**) reacted with Na[BH$_3$(CN)] to form the *exo*-allyl complex [Ru(η^3-CH$_2$$\cdots$CH$\cdots$CMe$_2$)(CO)($\eta$-C$_5H_5$)] (**12**), regioselective attack occurring on the methyl-substituted carbon as observed[10a] with the molybdenum complex [Mo(η^4-CH$_2$CHCMeCH$_2$)(CO)$_2$(η-C$_5$H$_5$)][PF$_6$]. Similarly, the cyclohexa-1,3-diene complex (**5**) reacted with Na[BH$_3$(CN)] in thf to form the η^3-cyclohexenyl complex (**13**) (Scheme 3). A single-crystal *X*-ray diffraction study was carried out with this complex so as to establish the conformation of the ring. Evaluation of proton–proton coupling constants would then be straightforward and thus allow a decision to be made as to which face of the C_6 ring is attacked by the nucleophilic reagent.

A perspective view of the molecule is shown in Figure 2 together with an atom numbering scheme. The crystal structure of **(13)** consists of isolated molecules separated by normal van der Waals contacts. The final non-hydrogen atom positional parameters are listed in Table 3, and the derived interatomic distances and interbond angles in Table 4. Each molecule shows the ruthenium atom to be co-ordinated to an η^5-cyclopentadienyl ligand [Ru–C 2.192(11)—2.261(10) Å], a linear carbonyl ligand [Ru–C(12) 1.831(11) Å, Ru–C(12)–O(1) 176.4(10)°], and an η^3-cyclohexenyl moiety [Ru–C(1) 2.208(13), Ru–C(2) 2.097(11), and Ru–C(3) 2.229(9) Å]. The cyclohexenyl ligand adopts the *exo* conformation with respect to the cyclopentadienyl group. The six-membered ring conformation is best described as boat-like. Thus torsion angles C(2)–C(1)–C(6)–C(5) and C(2)–C(3)–C(4)–C(5) are small, −2.0(17) and 0.5(13)° respectively (see also H–C–C–H angles given in Table 5). This ring conformation is in contrast to the chair-like conformer observed[2] in the solid-state structure of $[Mo(\eta^3\text{-}C_6H_9)(CO)_2(\eta\text{-}C_5H_5)]$. The difference is presumably dictated by intraligand steric effects. These would render a chair-like (and *exo*) conformation untenable for complex **(13)** due to contact between the CO ligand and the *endo*-hydrogen on C(5). For the molybdenum dicarbonyl species no such contact is forced on the chair-like conformer.

With the establishment of the solid-state structure it was then necessary to establish whether the conformation adopted by the C_6 ring in solution is the same as that in the solid state. This distinction can be made by consideration of the magnitude of the ^1H–^1H n.m.r. coupling between the allylic protons (H^1 and H^3) and the adjacent alkyl protons (4α, 4β, 6α, 6β) (Table 5). On the basis of the Karplus equation and the dihedral angles (φ) determined from the *X*-ray structure, for the boat form one such coupling would be expected of moderately large magnitude. In contrast, a chair conformation would show two fairly small couplings as demonstrated by the ^1H n.m.r. data reported for the related molybdenum complex $[Mo(\eta^3\text{-}C_6H_9)(CO)_2(\eta\text{-}C_5H_5)]$. These predictions are summarised in Table 6, together with the observed coupling constants. Inspection of the latter reveals that the conformation adopted by the cyclohexenyl ring in solution is the same as found in the solid state, *i.e.* a boat form.

Consideration of the dihedral angles between the protons on carbons 5 and 4 or 6 and the consequential expected couplings provides the basis for the assignment of the ^1H spectrum of complex **(13)**. From the dihedral angles obtained from the crystal structure determination, one large (> 10 Hz) vicinal coupling between the 5β and 4α protons (an axial–axial relationship) and one small (< 3 Hz) vicinal coupling between the 5α and 4β protons (an equatorial–equatorial relationship) is expected from the Karplus equation (see Table 6). The presence of one such small coupling (2.2 Hz) for the multiplet at δ 2.34—2.21 p.p.m. in the ^1H spectrum thus permits the signal's assignment to the 4,6β protons, whilst the signal at δ 2.09—1.92 p.p.m. with the large (10.7 Hz) coupling is assigned to the 4,6α protons.

With these assignments to hand it was possible to examine the stereoselectivity of the deuteride addition to the parent complex **(5)**. The ^2H n.m.r. spectrum of the η^3-cyclohexenyl complex obtained on addition of $Na[BD_3(CN)]$ to **(5)** exhibited

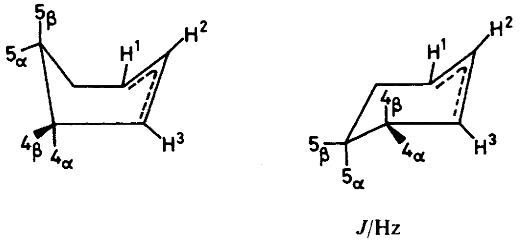
Table 3. Atomic co-ordinates (× 10^4) for complex **(13)**

Atom	*x*	*y*	*z*
Ru	2 232(1)	1 544(1)	1 490(1)
C(12)	2 109(14)	432(8)	2 451(9)
O(1)	1 934(14)	−257(7)	3 038(8)
C(7)	516(14)	2 974(8)	997(10)
C(8)	1 117(15)	2 693(9)	−52(11)
C(9)	395(17)	1 759(9)	−478(10)
C(10)	−658(16)	1 427(9)	294(11)
C(11)	−579(14)	2 168(10)	1 223(11)
C(1)	4 945(15)	1 047(10)	1 316(10)
C(2)	5 018(14)	1 978(9)	1 840(11)
C(3)	4 726(14)	2 062(7)	3 016(10)
C(4)	5 683(14)	1 265(8)	4 029(9)
C(5)	6 806(17)	526(10)	3 513(11)
C(6)	5 861(17)	156(9)	2 154(11)

Table 4. Bond lengths (Å) and angles (°) for complex **(13)**

Ru–C(12)	1.831(11)	Ru–C(7)	2.261(10)	C(8)–C(9)	1.372(16)	C(9)–C(10)	1.399(19)
Ru–C(8)	2.252(12)	Ru–C(9)	2.228(10)	C(10)–C(11)	1.409(17)	C(1)–C(2)	1.352(17)
Ru–C(10)	2.192(11)	Ru–C(11)	2.208(11)	C(1)–C(6)	1.530(16)	C(1)–H(1)	0.785(80)
Ru–C(1)	2.208(13)	Ru–C(2)	2.097(11)	C(2)–C(3)	1.389(18)	C(2)–H(2)	0.958(107)
Ru–C(3)	2.229(9)	C(12)–O(1)	1.149(15)	C(3)–C(4)	1.552(14)	C(3)–H(3)	1.070(93)
C(7)–C(8)	1.416(17)	C(7)–C(11)	1.414(17)	C(4)–C(5)	1.510(18)	C(5)–C(6)	1.542(16)
C(12)–Ru–C(7)	133.3(5)	C(12)–Ru–C(8)	155.3(4)	Ru–C(7)–C(11)	69.5(6)	C(8)–C(7)–C(11)	107.0(10)
C(7)–Ru–C(8)	36.6(4)	C(12)–Ru–C(9)	123.2(4)	Ru–C(8)–C(7)	72.1(6)	Ru–C(8)–C(9)	71.2(7)
C(7)–Ru–C(9)	60.8(4)	C(8)–Ru–C(9)	35.7(4)	C(7)–C(8)–C(9)	109.2(11)	Ru–C(9)–C(8)	73.1(6)
C(12)–Ru–C(10)	94.8(4)	C(7)–Ru–C(10)	61.3(4)	Ru–C(9)–C(10)	70.2(6)	C(8)–C(9)–C(10)	108.0(11)
C(8)–Ru–C(10)	60.6(4)	C(9)–Ru–C(10)	36.9(5)	Ru–C(10)–C(9)	73.0(6)	Ru–C(10)–C(11)	71.9(6)
C(12)–Ru–C(11)	99.5(5)	C(7)–Ru–C(11)	36.9(4)	C(9)–C(10)–C(11)	108.7(10)	Ru–C(11)–C(7)	73.6(6)
C(8)–Ru–C(11)	61.3(5)	C(9)–Ru–C(11)	61.9(5)	Ru–C(11)–C(10)	70.7(7)	C(7)–C(11)–C(10)	107.0(11)
C(10)–Ru–C(11)	37.3(5)	C(12)–Ru–C(1)	91.2(5)	Ru–C(1)–C(2)	67.3(7)	Ru–C(1)–C(6)	115.9(9)
C(7)–Ru–C(1)	134.7(5)	C(8)–Ru–C(1)	106.2(5)	C(2)–C(1)–C(6)	118.9(9)	Ru–C(1)–H(1)	108.3(51)
C(9)–Ru–C(1)	105.9(4)	C(10)–Ru–C(1)	134.8(4)	C(2)–C(1)–H(1)	117.1(55)	C(6)–C(1)–H(1)	118.0(54)
C(11)–Ru–C(1)	167.0(4)	C(12)–Ru–C(2)	109.4(4)	Ru–C(2)–C(1)	76.2(7)	Ru–C(2)–C(3)	76.5(7)
C(7)–Ru–C(2)	106.6(4)	C(8)–Ru–C(2)	94.8(4)	C(1)–C(2)–C(3)	118.6(11)	Ru–C(2)–H(2)	95.3(64)
C(9)–Ru–C(2)	116.3(5)	C(10)–Ru–C(2)	152.9(5)	C(1)–C(2)–H(2)	116.2(66)	C(3)–C(2)–H(2)	120.3(71)
C(11)–Ru–C(2)	142.2(5)	C(1)–Ru–C(2)	36.5(5)	Ru–C(3)–C(2)	66.2(5)	Ru–C(3)–C(4)	116.5(6)
C(12)–Ru–C(3)	88.9(4)	C(7)–Ru–C(3)	102.7(3)	C(2)–C(3)–C(4)	117.1(9)	Ru–C(3)–H(3)	118.5(43)
C(8)–Ru–C(3)	114.2(4)	C(9)–Ru–C(3)	147.4(4)	C(2)–C(3)–H(3)	123.0(55)	C(4)–C(3)–H(3)	109.7(47)
C(10)–Ru–C(3)	160.4(4)	C(11)–Ru–C(3)	123.1(4)	C(3)–C(4)–C(5)	110.8(9)	C(4)–C(5)–C(6)	115.2(9)
C(1)–Ru–C(3)	64.2(4)	C(2)–Ru–C(3)	37.3(5)	C(1)–C(6)–C(5)	110.1(10)		
Ru–C(12)–O(1)	176.4(10)	Ru–C(7)–C(8)	71.4(6)				

Table 5. Calculated and observed allylic–alkyl proton couplings for $[Ru(\eta^3\text{-}C_6H_9)(CO)(\eta\text{-}C_5H_5)]$ and $[Mo(\eta^3\text{-}C_6H_9)(CO)_2(\eta\text{-}C_5H_5)]$



	Dihedral angle $\varphi^a/^\circ$	J/Hz calc.^{b}	J/Hz obs.
(*i*) $[Ru(\eta^3\text{-}C_6H_9)(CO)(\eta\text{-}C_5H_5)]$			
$H^{4\alpha}$–H^3	93.7	0	0
$H^{6\alpha}$–H^1	90.1	0	
$H^{4\beta}$–H^3	25.9	8.1	6.6
$H^{6\beta}$–H^1	29.8	7.5	
(*ii*) $[Mo(\eta^3\text{-}C_6H_9)(CO)_2(\eta\text{-}C_5H_5)]^c$			
$H^{4\alpha}$–H^3	47.9	4.5	1.9
$H^{6\alpha}$–H^1	56.8	3.0	
$H^{4\beta}$–H^3	70.4	1.1	1.8
$H^{6\beta}$–H^1	60.8	2.4	

^{a} From X-ray data. ^{b} J(HH) = $10\cos^2\varphi$ for $0 < \varphi < 90^\circ$, $16\cos^2\varphi$ for $90 < \varphi < 180^\circ$. ^{c} Angles φ calculated from atomic co-ordinates listed in ref. 2.

Table 6. Calculated and observed alkyl–alkyl proton couplings for $[Ru(\eta^3\text{-}C_6H_9)(CO)(\eta\text{-}C_5H_5)]$

	Dihedral angle $\varphi^a/^\circ$	J/Hz calc.^{b}	J/Hz obs.
$H^{4\alpha}$–$H^{5\beta}$	161.3	14.4	10.7
$H^{6\alpha}$–$H^{5\beta}$	162.8	14.6	
$H^{4\beta}$–$H^{5\alpha}$	76.6	0.5	2.2
$H^{6\beta}$–$H^{5\alpha}$	75.3	0.6	
$H^{4\alpha}$–$H^{5\alpha}$	43.0	5.3	5.0
$H^{6\alpha}$–$H^{5\alpha}$	44.5	5.1	
$H^{4\beta}$–$H^{5\beta}$	41.7	5.6	7.6
$H^{6\beta}$–$H^{5\beta}$	43.0	5.3	

^{a} From X-ray data. ^{b} Calculated as in Table 5.

one strong resonance at δ 2.31 p.p.m. corresponding to the 4,6β position, together with a much weaker signal at δ 2.01 p.p.m. (4,6α position), thus showing that 'D^-' is delivered selectively (90—95%) to the opposite face (*exo*) of the C_6 ring to which the ruthenium is co-ordinated. This positive identification of *exo* attack is consistent with observations made on both molybdenum[2] and manganese[20] systems.

One additional feature relative to this reaction, which merits comment, is that prior to chromatographic work-up the reaction mixture appeared yellow in colour. However, contact with alumina induced a rapid change to the deep blue colour of the isolated product (**13**), accompanied by the evolution of a gas derived from the cyanoborohydride residue. Coupled with this behaviour is the observation that addition of $Na[BH_3(CN)]$ to a suspension of complex (**5**) in $[^2H_8]$tetrahydrofuran contained in a n.m.r. tube led to the rapid appearance of a signal at δ −8.97 p.p.m. in the ^1H spectrum of the resultant yellow solution. A hydride intermediate is therefore implicated in the formation of (**13**), and it is suggested that this species is a borane adduct of the η^3-cyclohexenyl complex. Such intermediates have been postulated previously[21] in borohydride reductions, most notably in the conversion of co-ordinated CO in metal-bound formyl groups. It can thus be envisaged that a $BH_2(CN)$ moiety, being a strong Lewis acid, is able to interact with the π-electron system of the C_6 ring and/or the metal centre. Unfortunately attempts to obtain suitable crystals for X-ray work on this adduct were unsuccessful. However, such behaviour would seem to reinforce the idea that the action of nucleophilic reagents such as $Na[BH_3(CN)]$ on metal complexes is rather more subtle than was hitherto appreciated.

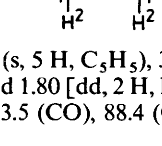
Finally the reaction of the cyclo-octa-1,5-diene complex (**8**) with $Na[BH_3(CN)]$ was studied. At 0 °C in thf, yellow crystals of (**14**) were obtained. Examination of the i.r., mass, ^1H and $^{13}C\text{-}\{^1H\}$ n.m.r. spectra showed that the molecule has the illustrated structure where the C_8H_{13} ring is bonded in a 1,4,5-η^3 mode to a $Ru(CO)(\eta\text{-}C_5H_5)$ fragment. This complex did not isomerise to a 1,2,3-η^3-allyl species. It is of interest that a ruthenium 1,4,5-η^3-C_8H_{13} system is postulated[22] as an intermediate in the reaction of $[RuH_2(PPh_3)_4]$ with cyclo-octa-1,5-diene.

Experimental

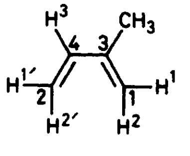
The ^1H and $^{13}C\text{-}\{^1H\}$ n.m.r. spectra were recorded on JEOL FX 90Q and FX 200 spectrometers, as appropriate. Data are given for room-temperature measurements and coupling constants are in Hz. Carbon-13 chemical shifts are relative to $SiMe_4$ with positive values to high frequency of the reference. I.r. spectra were recorded on a Perkin-Elmer 257 spectrophotometer. All reactions were carried out in Schlenk tubes (unless otherwise stated) under an atmosphere of dry oxygen-free nitrogen, using freshly distilled solvents.

Preparation of $[Ru(NCMe)_2(CO)(\eta\text{-}C_5H_5)][BF_4]$ (**1**).—A solution of $[Ru(NCMe)(CO)_2(\eta\text{-}C_5H_5)][BF_4]$[23] (3.05 g, 8.71 mmol) in acetonitrile (70 cm^3) in a water-cooled quartz vessel was irradiated with u.v light (Hanovia 500-W lamp) for 16 h. Solvent was then removed *in vacuo*, the residue dissolved in CH_2Cl_2, and diethyl ether added, affording a bright yellow-orange precipitate of complex (**1**) (2.75 g, 87%) (Found: C, 33.2; H, 2.8; N, 7.8. $C_{10}H_{11}BF_4N_2ORu$ requires C, 33.1; H, 3.1; N, 7.7%); ν(CO) (CH_2Cl_2) 2 000s cm^{-1}. N.m.r. (CD_3NO_2): ^1H, δ 5.23 (s, 5 H, C_5H_5) and 2.46 (s, 6 H, CH_3); $^{13}C\text{-}\{^1H\}$, δ 198.1 (CO), 129.2 (CCH_3), 82.1 (C_5H_5), and 4.5 p.p.m. (CH_3).

Preparation of $[Ru(\eta^4\text{-}CH_2{=}CHCH{=}CH_2)(CO)(\eta\text{-}C_5H_5)][BF_4]$ (**2**).—Buta-1,3-diene (*ca.* 50 mmol) was condensed (−196 °C) into a Young's tube containing a solution of complex (**1**) (0.70 g, 1.93 mmol) in CH_2Cl_2 (50 cm^3). The tube was then sealed and the reaction mixture stirred at room temperature for 3 d, after which the volume of solution was reduced *in vacuo* and diethyl ether added to afford white *crystals* of complex (**2**) (0.55 g, 85%) (Found: C, 35.3; H, 3.3. $C_{10}H_{11}BF_4ORu$ requires C, 35.6; H, 3.3%); ν(CO) (CH_2Cl_2) 2 045s cm^{-1}. N.m.r. (CD_3NO_2): ^1H, δ 6.12 [unresolved multiplet (um), 2 H, H^3], 5.79 (s, 5 H, C_5H_5), 3.82 [dd, 2 H, H^1, $J(H^1H^3)$ 8.8, $J(H^1H^2)$ 2.2], and 1.80 [dd, 2 H, H^2, $J(H^2H^3)$ 10.1, $J(H^2H^1)$ 2.2]; $^{13}C\text{-}\{^1H\}$, δ 203.5 (CO), 88.4 (C_5H_5), 86.6 (C^2), and 50.4 p.p.m. (C^1).



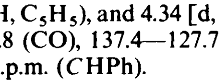
Preparation of [Ru{η^4-CH$_2$=C(CH$_3$)CH=CH$_2$}(CO)(η-C$_5$H$_5$)][BF$_4$] (**3**).—A solution of complex (**1**) (1.00 g, 2.75 mmol) in CH$_2$Cl$_2$ (50 cm^3) was stirred with isoprene (5.5 cm^3, 55 mmol) for 3 d at room temperature. The volume was reduced *in vacuo* and diethyl ether slowly added, affording white *crystals* of complex (**3**) (0.82 g, 85%) (Found: C, 38.1; H, 3.6. C$_{11}$H$_{13}$BF$_4$ORu requires C, 37.8; H, 3.8%); ν(CO) (CH$_2$Cl$_2$) 2 045s cm^{-1}. N.m.r. (CD$_3$NO$_2$): ^{1}H, δ 6.06 (um, 1 H, H^3), 5.70 (s, 5 H, C$_5$H$_5$), 3.79 (um, 2 H, H^1, H$^{1'}$), 2.46 (s, 3 H, CH$_3$), and 1.63 (um, 2 H, H^2, H$^{2'}$); ^{13}C-{^{1}H}, δ 203.5 (CO), 109.3 (C^4), 89.5 (C$_5$H$_5$), 87.1 (C^3), 49.9 (C^2), 48.1 (C^1), and 24.5 p.p.m. (CH$_3$).



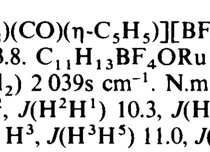
The following cations were synthesised in a similar manner.

[Ru(η^4-CHPh=CHCH=CHPh)(CO)(η-C$_5$H$_5$)][BF$_4$] (**4**). Yield 73% (Found: C, 53.9; H, 4.0. C$_{22}$H$_{19}$BF$_4$ORu requires C, 54.2; H, 3.9%); ν(CO) (CH$_2$Cl$_2$) 2 030s cm^{-1}. N.m.r. [(CD$_3$)$_2$CO]: ^{1}H, δ 7.51 (um, 10 H, Ph), 7.16 [d, 2 H, CH, J(HH) 9.8], 5.73 (s, 5 H, C$_5$H$_5$), and 4.34 [d, 2 H, C*H* Ph, J(HH) 9.8]; ^{13}C-{^{1}H}, δ 204.8 (CO), 137.4—127.7 (Ph), 89.9 (C$_5$H$_5$), 79.9 (CH), and 76.8 p.p.m. (*C*HPh).

[Ru(η^4-C$_6$H$_8$)(CO)(η-C$_5$H$_5$)][BF$_4$] (**5**). Yield 70% (Found: C, 39.7; H, 3.5. C$_{12}$H$_{13}$BF$_4$ORu requires C, 39.9; H, 3.6%); ν(CO) (CH$_2$Cl$_2$) 2 037s cm^{-1}. N.m.r. [(CD$_3$)$_2$CO]: ^{1}H, δ 6.28 {q, [AX]$_2$, 2 H, H^1, J(AX) 7.2, J(AA′) 2.2}, 5.89 (s, 5 H, C$_5$H$_5$), 5.07 (m, 2 H, H^2), and 1.91 [dd, 4 H, H^3, J(H^{3}H^2) 0.7, J(H^{3}H$^{3'}$) 1.0]; ^{13}C-{^{1}H}, δ 204.5 (CO), 87.8 (C$_5$H$_5$), 81.7 (C^1), 77.2 (C^2), and 22.3 p.p.m. (C^3).

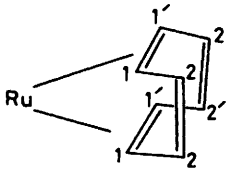


[Ru(η^4-*trans*-C$_5$H$_8$)(CO)(η-C$_5$H$_5$)][BF$_4$] (**6a**). Yield 82% (Found: C, 38.0; H, 3.8. C$_{11}$H$_{13}$BF$_4$ORu requires C, 37.8; H, 3.8%); ν(CO) (CH$_2$Cl$_2$) 2 039s cm^{-1}. N.m.r.: ^{1}H [(CD$_3$)$_2$CO], δ 6.30 [qdd, 1 H, H^2, J(H^{2}H^1) 10.3, J(H^{2}H^3) 5.6, J(H^{2}CH$_3$) 0.7], 6.13 [dddd, 1 H, H^3, J(H^{3}H^5) 11.0, J(H^{3}H^4) 8.1, J(H^{3}H^2) 5.6, J(H^{3}H^1) 0.8], 5.93 (s, 5 H, C$_5$H$_5$), 3.68 [ddd, 1 H, H^4, J(H^{4}H^3) 8.1, J(H^{4}H^5) 2.0, J(H^{4}H^2) 0.7], 3.07 [ddq, 1 H, H^1, J(H^{1}H^2) 10.3, J(H^{1}CH$_3$) 6.1, J(H^{1}H^3) 0.8], 2.00 [ddd, 1 H, H^5, J(H^{5}H^3) 11.0, J(H^{5}H^4) 2.0, J(H^{5}H^2) 0.9], and 1.85 [dd, 3 H, CH$_3$, J(CH$_3$H^1) 6.1, J(CH$_3$H^2) 0.7]; ^{13}C-{^{1}H} (CD$_3$NO$_2$), δ 204.6 (CO), 88.3 (C$_5$H$_5$), 88.1 (C^3), 83.3 (C^2), 76.5 (C^4), 48.6 (C^1), and 20.7 p.p.m. (CH$_3$).

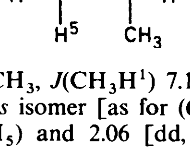


[Ru(η^4-1,5-C$_8$H$_{12}$)(CO)(η-C$_5$H$_5$)][BF$_4$] (**8**). Yield 51% (Found: C, 42.6; H, 4.6. C$_{14}$H$_{17}$BF$_4$ORu requires C, 43.2; H, 4.4%); ν(CO) (CH$_2$Cl$_2$) 2 019s cm^{-1}. N.m.r. [(CD$_3$)$_2$CO]: ^{1}H, δ 5.80 (s, 5 H, C$_5$H$_5$), 5.55 (um, 2 H, CH), 4.72 (um, 2 H, CH), 2.66 (um, 2 H, CH$_2$), and 2.37 (um, 2 H, CH$_2$); ^{13}C-{^{1}H}, δ 207.5 (CO), 88.3 (C$_5$H$_5$), 87.9 (CH), 86.7 (CH), 31.50 (CH$_2$), and 28.6 p.p.m. (CH$_2$).

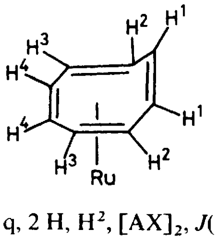
[Ru(η^4-C$_8$H$_8$)(CO)(η-C$_5$H$_5$)][BF$_4$] (**9**). Yield 51% (Found: C, 43.7; H, 3.5. C$_{14}$H$_{13}$BF$_4$ORu requires C, 43.7; H, 3.4%); ν(CO) (CH$_2$Cl$_2$) 2 040s cm^{-1}. N.m.r. [(CD$_3$)$_2$CO]: ^{1}H, δ 6.37 [t, 2 H, H$^{2'}$, J(H$^{2'}$H$^{1'}$) 1.2], 6.04 [t, 2 H, H^2, J(H^{2}H^1) 1.2], 5.85 (s, 5 H, C$_5$H$_5$), 5.79 [dt, 2 H, H$^{1'}$, J(H$^{1'}$H^1) 8.3, J(H$^{1'}$H$^{2'}$) 1.2], and 5.16 [dt, 2 H, H^1, J(H^{1}H$^{1'}$) 8.3, J(H^{1}H^2) 1.2]; ^{13}C-{^{1}H}, δ 207.1 (CO), 135.9 (C$^{2'}$), 134.1 (C^2), 91.9 (C$^{1'}$), 89.8 (C^1), and 89.2 p.p.m. (C$_5$H$_5$).



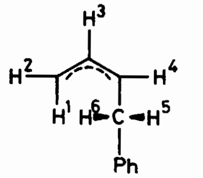
Reaction of Complex (**1**) *with* cis-*Penta*-1,3-*diene*.—A solution of complex (**1**) (0.75 g, 2.07 mmol) in CH$_2$Cl$_2$ (50 cm^3) was stirred with *cis*-penta-1,3-diene for 7 d at room temperature. The solution was then reduced in volume *in vacuo* and diethyl ether slowly added, affording an off-white precipitate. Subsequent recrystallisation from dichloromethane–ether yielded a white crystalline solid (0.16 g, 22%) (Found: C, 37.6; H, 4.0. C$_{11}$H$_{13}$BF$_4$ORu requires C, 37.8; H, 3.8%); ν(CO) (CH$_2$Cl$_2$) 2 035s cm^{-1}. N.m.r. (CD$_3$NO$_2$): ^{1}H, major *cis* isomer (**7a**), δ 6.06 (um, 2 H, H^2, H^3), 5.76 (s, 5 H, C$_5$H$_5$), 5.02 (um, 1 H, H^1), 3.89 [ddd, 1 H, H^4, J(H^{4}H^3) 8.2, J(H^{4}H^5) 2.7, J(H^{4}H^2) 0.7], 2.53 [ddd, 1 H, H^5, J(H^{5}H^3) 11.6, J(H^{5}H^4) 2.7, J(H^{5}H^2) 1.0], and 1.34 [dd, 3 H, CH$_3$, J(CH$_3$H^1) 7.1, J(CH$_3$H^2) 0.7]; also observed, major *trans* isomer [as for (**6a**)]; minor *cis* isomer (**7b**), δ 5.84 (s, C$_5$H$_5$) and 2.06 [dd, CH$_3$, J(CH$_3$H^1) 7.8, J(CH$_3$H^2) 0.7]; minor *trans* isomer (**6b**), δ 5.46 (s, C$_5$H$_5$); ^{13}C-{^{1}H}, *major cis* isomer (**7a**), δ 204.9 (CO), 89.1 (C^3), 88.9 (C$_5$H$_5$), 85.0 (C^2), 74.4 (C^4), 51.2 (C^1), and 16.7 (CH$_3$); also observed, major *trans* isomer [as for (**6a**)]; minor *cis* isomer (**7b**), δ 98.9 (C^3), 90.5 (C$_5$H$_5$), 81.7 (C^2), 79.5 (C^4), 53.1 (C^1), and 18.3 (CH$_3$); minor *trans* isomer (**6b**), δ 94.5 (C^3), 91.4 (C$_5$H$_5$), 79.7 (C^2 or C^4), and 19.3 p.p.m. (CH$_3$).



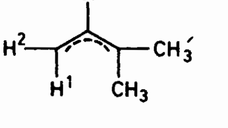
Preparation of [Ru(η^6-C$_8$H$_8$)(η-C$_5$H$_5$)][BF$_4$] (**10**).—A solution of complex (**9**) (0.08 g, 0.21 mmol) in CH$_2$Cl$_2$ (20 cm^3, Pyrex vessel) was irradiated with u.v. light (500 W) for 18 h. The solution was then reduced in volume *in vacuo* and diethyl ether slowly added to afford a cream, crystalline solid, (**10**) (0.07 g, 94%) (Found: C, 44.5; H, 3.9. C$_{13}$H$_{13}$BF$_4$Ru requires C, 43.7; H, 3.7%). N.m.r. [(CD$_3$)$_2$CO]: ^{1}H, δ 6.96 {q, 2 H, H^1, [AX]$_2$, J(AA′) 7.7, J(AX) 6.6}, 6.07 {q, 2 H, H^2, [AX]$_2$, J(AA′) 7.7, J(AX) 6.6}, 6.02 (um, 2 H, H^3), 5.74 (s, 5 H, C$_5$H$_5$), and 5.13 (um, 2 H, H^4); ^{13}C-{^{1}H}, δ 134.8 (C^1), 103.5 (C^2), 93.8 (C^3), 87.2 (C$_5$H$_5$), and 83.0 p.p.m. (C^4).



Preparation of [Ru(η^3-CH$_2$CHCHCH$_2$Ph)(CO)(η-C$_5$H$_5$)] (**11**).—Lithium diphenylcuprate [CuBr (0.12 g, 0.86 mmol), LiPh (1.72 mmol)] in diethyl ether (2 cm^3) was added to a suspension of complex (**2**) (0.30 g, 0.86 mmol) in thf (10 cm^3) at −78 °C. After stirring for 15 min at this temperature the reaction mixture was allowed to warm to room temperature and solvent removed *in vacuo*. The brown residue was extracted into diethyl ether and chromatographed on alumina, elution with hexane affording a yellow band. Recrystallisation (−78 °C) from hexane gave white *crystals* of complex (**11**) (0.10 g, 34%) (Found: C, 59.3; H, 4.8%; *M* 326. $C_{16}H_{16}ORu$ requires C, 59.0; H, 5.0%; *M* 326); ν(CO) (CH_2Cl_2) 1 929s cm^{-1}. N.m.r. (C_6D_6): ^1H, δ 7.16 (um, 5 H, Ph), 4.47 (s, 5 H, C_5H_5), 3.89 (um, 1 H, H^3), 3.55 (um, 1 H, H^4), 2.97 (um, 2 H, H^2, H^5), 2.21 [dd, 1 H, H^6, $J(H^6H^5)$ 14.2, $J(H^6H^4)$ 10.7], and 1.94 [dd, 1 H, H^1, $J(H^1H^3)$ 11.1, $J(H^1H^2)$ 2.0]; ^{13}C-{^1H}, δ 208.2 (CO), 144.9 (C_{ipso}), 129.1—126.1 (C_6H_5), 82.1 (C_5H_5), 66.2 (CH), 53.0 ($CHCH_2$), 40.0 (CH_2), and 31.1 p.p.m. (CH_2Ph).



Preparation of [Ru($η^3$-CH_2CHCMe_2)(CO)(η-C_5H_5)] (**12**).—To a suspension of complex (**3**) (0.40 g, 1.15 mmol) in thf (10 cm^3), Na[BH_3(CN)] (0.072 g, 1.15 mmol) was added at 0 °C and the mixture stirred at this temperature for 30 min, whereupon a yellow solution was obtained. Volatiles were then removed *in vacuo* and the yellow-brown residue extracted into CH_2Cl_2 and chromatographed on an alumina/hexane column. Elution with diethyl ether afforded a blue band, recrystallisation of which (hexane, −78 °C) gave blue *crystals* of complex (**12**) (0.03 g, 10%) (Found: C, 50.2; H, 5.6. $C_{11}H_{14}ORu$ requires C, 50.2; H, 5.7%); ν(CO) (CH_2Cl_2) 1 923s cm^{-1}. N.m.r. (C_6D_6): ^1H, δ 4.46 (s, 5 H, C_5H_5), 3.60 [dd, 1 H, H^3, $J(H^3H^1)$ 11.0, $J(H^3H^2)$ 7.1], 2.79 [dd, 1 H, H^2, $J(H^2H^3)$ 7.1, $J(H^2H^1)$ 2.2], 1.66 [dd, 1 H, H^1, $J(H^1H^3)$ 11.0, $J(H^1H^2)$ 2.2], 1.61 (s, 3 H, CH_3'), and 1.29 p.p.m. (s, 3 H, CH_3).



Preparation of [Ru($η^3$-C_6H_9)(CO)(η-C_5H_5)] (**13**).—This complex was prepared as for (**12**) from (**5**) (0.50 g, 1.39 mmol) and Na[BH_3(CN)] (0.087 g, 1.39 mmol). Subsequent to chromatography, recrystallisation from hexane (−78 °C) afforded blue *crystals* of (**13**) (0.08 g, 20%) (Found: C, 51.9; H, 5.7%; *M* 276. $C_{12}H_{14}ORu$ requires C, 52.4; H, 5.1%; *M* 276); ν(CO) (CH_2Cl_2) 1 921s cm^{-1}. N.m.r. (C_6D_6): ^1H, δ 4.60 (s, 5 H, C_5H_5), 2.28 [dddd, 2 H, $H^{4\beta}$, $H^{6\beta}$, $J(H^{4\beta,6\beta}H^{4\alpha,6\alpha})$ 16.2, $J(H^{4\beta,6\beta}H^{5\beta})$ 7.6, $J(H^{4\beta,6\beta}H^{3,1})$ 6.6, $J(H^{4\beta,6\beta}H^{5\alpha})$ 2.2], 2.01 [ddd, 2 H, $H^{4\alpha}$, $H^{6\alpha}$, $J(H^{4\alpha,6\alpha}H^{4\beta,6\beta})$ 16.2, $J(H^{4\alpha,6\alpha}H^{5\beta})$ 10.7, $J(H^{4\alpha,6\alpha}H^{5\alpha})$ 6.0], 1.42 [ttd, 1 H, $H^{5\alpha}$, $J(H^{5\alpha}H^{5\beta})$ 13.2, $J(H^{5\alpha}H^{4\alpha,6\alpha})$ 6.0, $J(H^{5\alpha}H^{4\beta,6\beta})$ 2.2], and 1.20 [ttd, 1 H, $H^{5\beta}$, $J(H^{5\beta}H^{5\alpha})$ 13.2, $J(H^{5\beta}H^{4\alpha,6\alpha})$ 10.7, $J(H^{5\beta}H^{4\beta,6\beta})$ 7.6]; ^{13}C-{^1H}, δ 210.4 (CO), 82.0 (C_5H_5), 69.3 (C^2), 48.1 (C^1, C^3), 28.4 (C^4, C^6), and 20.1 p.p.m. (C^5); [Ru($η^3$-C_6H_8D)(CO)(η-C_5H_5)], ^2D, δ 2.31 p.p.m. (s, $H^{4\beta}$, $H^{6\beta}$).

Preparation of [Ru{-$CH(CH_2)_3CH{=}CHCH_2CH_2$}(CO)(η-$C_5H_5$)] (**14**).—This was prepared as for (**12**) from (**8**) (0.112 g, 0.29 mmol) and Na[BH_3(CN)] (0.020 g, 0.32 mmol). After chromatography recrystallisation from hexane (−78 °C) afforded yellow *crystals* of complex (**14**) (0.075 g, 86%) (Found: C, 55.0; H, 5.8%, *M* 304. $C_{14}H_{18}ORu$ requires C, 55.4; H, 6.0%; *M* 304); ν(CO) (CH_2Cl_2) 1 921s cm^{-1}. N.m.r. (C_6D_6): ^1H, δ 4.66 (um, 1 H, CH), 4.49 (s, 5 H, C_5H_5), 4.30 (um, 1 H, CH), 3.09 (um, 1 H, RuCH), 2.64 (um, 2 H, CH_2), and 1.94 (um, 8 H, CH_2); ^{13}C-{^1H}, δ 211.1 (CO), 85.9 (C_5H_5), 72.5 (CH), 67.3 (CH), 47.3 (CH_2), 40.2 (CH_2), 29.7 (CH_2), 27.9 (CH_2), 25.3 (CH_2), and 21.1 p.p.m. (RuCH).

Crystal Structure Analysis.—Structure analyses were carried out by *X*-ray diffraction methods at room temperature using a Nicolet *P*3*m* diffractometer on single crystals of complexes (**5**) and (**13**) sealed in thin-walled glass capillaries under N_2. Intensity data were collected by variable speed (2.5—29.3° min^{-1}) θ—2θ scans [width 2.4° + $\Delta_{\alpha_1\alpha_2}$ for (**5**) and 3.0° + $\Delta_{\alpha_1\alpha_2}$ for (**13**)] for the unique portions of reciprocal space in the range $4 < 2\theta < 50°$. In each case the intensities of three standard reflections were remeasured after every 100 intensity measurements and showed a small decay [2.8% for (**5**) and 1% for (**13**)]; the remaining intensity data were corrected accordingly. Absorption corrections were applied to the data set for complex (**5**) by Gaussian quadrature based on the crystal faces [and perpendicular distances (mm) from an origin] (−10−3)[0.125], (−20−3)[0.115], (−101)[0.1375], (001)[0.1325], (101)[0.125], (10−1)[0.1375], (00−1)[0.1325], (010)[0.175], and (0−10)[0.175] giving transmission coefficients between 0.787 and 0.710. The structure solution in both cases was carried out by conventional Patterson and Fourier techniques. For complex (**5**), of 1 819 intensity data recorded, 1 606 remained after averaging of symmetry-related and duplicate measurements; of these 1 373 with $I > 2\sigma(I)$ were used in refinement of the structure. All atoms bar two cyclopentadienyl-group hydrogens were located on difference electron-density syntheses. The structure was refined in the centrosymmetric space group *Pnma* with atoms Ru, C(4), H(4), C(7), O, B, F(2), and F(3) constrained to lie on the mirror plane. Cyclopentadienyl-group hydrogens were constrained to idealised geometries with C–H 0.96 Å, and assigned fixed isotropic vibrational parameters *ca.* 1.2 times that of their attached carbon atom; other hydrogens were refined isotropically without constraints. All other atoms except B were refined with anisotropic vibrational parameters. Final residual indices* were $R = 0.040$, $R' = 0.041$, and $S = 2.2$ with weight, $w = [\sigma_c^2(F_o) + 0.0002F_o^2]^{-1}$. A final difference electron-density map showed no features of chemical significance, the largest (1.1 e $Å^{-3}$) being close to the BF_4 anion. Of the 2 126 intensity data recorded for complex (**13**), 1 862 remained after averaging of duplicate and symmetry-related measurements; of these, 1 492 with $I > 2\sigma(I)$ were used in the refinement of the structure.

The analysis for complex (**13**) proceeded as for (**5**) with all but three cyclopentadienyl hydrogens located directly, and only the allylic hydrogens refined without constraints. No positional constraints were applied to the heavy-atom positions, all such atoms being refined anisotropically. Final residual indices were $R = 0.070$, $R' = 0.069$, and $S = 1.71$ with weights, $w = [\sigma_c^2(F_o) + 0.0015F_o^2]$. The final electron-density map showed residual features within 1 Å of the ruthenium atom of magnitude +2.4 and −1.5 e $Å^{-3}$.

All calculations were carried out with the SHELXTL program package[24] on the Nicolet *R3m/E* system, using the complex neutral scattering factors of ref. 25.

Crystal data for complex (**5**). $C_{12}H_{13}BF_4ORu$, $M = 361.1$, orthorhombic, space group *Pnma* (by refinement), $a =$

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* $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $R' = \Sigma w^{\frac{1}{2}}||F_o| - |F_c||/\Sigma w^{\frac{1}{2}}|F_o|$; $S = |\Sigma w(|F_o| - |F_c|)^2/(N_o - N_v)|^{\frac{1}{2}}$; where N_v is the number of least-squares variables [1 101 for (**5**) and 139 for (**13**)].

11.246(6), b = 9.297(4), c = 12.541(5) Å, U = 1 311(1) Å^3, Z = 4, D_c = 1.83 g cm^{-3}, $F(000)$ = 712 electrons, graphite-monochromated X-radiation, $\bar{\lambda}$ = 0.710 69 Å, μ(Mo-K_α) = 12.2 cm^{-1}.

Crystal data for complex (**13**). $C_{12}H_{14}ORu$, M = 275.2, monoclinic, space group $P2_1/c$, a = 7.530(8), b = 13.193(9), c = 11.084(5) Å, β = 107.27(6)°, U = 1 051(1) Å^3, Z = 4, D_c = 1.74 g cm^{-3}, $F(000)$ = 552 electrons, graphite-monochromated X-radiation, $\bar{\lambda}$ = 0.710 69 Å, μ(Mo-K_α) = 14.3 cm^{-1}.

Acknowledgements

We thank the S.E.R.C. for support, B.P. (Sunbury) for a C.A.S.E. Studentship (to M. C.), and Drs. P. Lodge (B.P.) and M. Murray for helpful discussions.

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Received 12*th December* 1984; *Paper* 4/2107