In memory of T. A. Stephenson

Reactions of Co-ordinated Ligands. Part 42.[1] The Synthesis and Reactions of Cationic η^4-Tetraphenylcyclobutadieneruthenium Complexes; *X*-Ray Crystal Structures of $[Ru(NCMe)(\eta^4\text{-}C_4Ph_4)(\eta\text{-}C_5H_5)][BF_4]$ and $[Ru\{\eta^5\text{-}CH(Ph)C(Ph)C(Ph)C(Ph)O\}(\eta\text{-}C_5H_5)]$ *

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Addition of $Ag[BF_4]$ to a solution of $[Ru_2(CO)_4(\eta\text{-}C_5H_5)_2]$ and PhC_2Ph in CH_2Cl_2 results in the formation of the η^4-cyclobutadiene complex $[Ru(CO)(\eta^4\text{-}C_4Ph_4)(\eta\text{-}C_5H_5)][BF_4]$ (**1**). U.v. irradiation of a solution of (**1**) in MeCN gives $[Ru(NCMe)(\eta^4\text{-}C_4Ph_4)(\eta\text{-}C_5H_5)][BF_4]$ (**2**), structurally identified by *X*-ray crystallography. The η^4-tetraphenylcyclobutadiene ligand is not co-ordinated symmetrically to the ruthenium as is indicated by Ru–C distances of 2.192(2), 2.208(3), 2.177(2), and 2.175(2) Å, a distortion which is related to the frontier orbitals presented by the d^6 $Ru(\eta\text{-}C_5H_5)\text{-}L^+$ fragment (L = MeCN). The mechanism of formation of (**1**) is discussed. Tetramethylammonium bromide and chloride also react with (**1**) on u.v. irradiation in CH_2Cl_2 to form $[RuX(\eta^4\text{-}C_4Ph_4)(\eta\text{-}C_5H_5)]$ [X = Br (**4**) or Cl (**5**)]. These complexes are also formed when (**2**) is reacted thermally with the corresponding halide anions. A related reaction occurs between (**2**) and the thiolate anion of $Na[SC_6H_4Me\text{-}4]$ forming $[Ru(SC_6H_4Me\text{-}4)(\eta^4\text{-}C_4Ph_4)(\eta\text{-}C_5H_5)]$, however, the presence of water in this latter reaction leads to an unusual ring-opening reaction and the formation of $[Ru\{\eta^5\text{-}CH(Ph)C(Ph)C(Ph)C(Ph)O\}(\eta\text{-}C_5H_5)]$ (**7**) whose structure was elucidated by *X*-ray crystallography. A η^5(5 e)-bonded butadienolato ligand has been generated by nucleophilic attack of hydroxide ion on the $\eta^4\text{-}C_4Ph_4$ ligand leading to ring-opening of an η^3-cyclobutenyl complex. Protonation of (**7**) affords $[Ru\{\eta^6\text{-}C_6H_5(CH_2CPh{=}CPhCOPh)\}(\eta\text{-}C_5H_5)][BF_4]$ (**8**). Mixed C_5–C_6 sandwich cations are also formed on u.v. irradiation of (**1**) in the presence of alkynes RC_2R, and in this way $[Ru(\eta^6\text{-}C_6Ph_6)(\eta\text{-}C_5H_5)][BF_4]$ (**9**), $[Ru(\eta^6\text{-}C_6Ph_5Me)(\eta\text{-}C_5H_5)][BF_4]$ (**10**), $[Ru(\eta^6\text{-}C_6Ph_4Me_2)(\eta\text{-}C_5H_5)][BF_4]$ (**11**), and $[Ru\{\eta^6\text{-}C_6Ph_4(CO_2Me)_2\}(\eta\text{-}C_5H_5)][BF_4]$ (**12**) are obtained in good to moderate yield. Complex (**9**) is also formed on reaction of (**5**) with PhC_2Ph and $Ag[BF_4]$, providing insight into this novel ring-expansion reaction. The related cationic complex $[Ru(\eta^6\text{-}C_6Et_6)(\eta\text{-}C_5H_5)][BF_4]$ (**13**) is formed in low yield on reaction of EtC_2Et with $[Ru_2(CO)_4(\eta\text{-}C_5H_5)_2]$ and $Ag[BF_4]$. The low-temperature 100.6-MHz $^{13}C\text{-}\{^1H\}$ n.m.r. spectrum of (**13**) is discussed in terms of rotational movement of the ethyl groups. Treatment of (**9**) and (**11**) with $K[BHBu^s_3]$ leads to selective attack on the η-cyclopentadienyl ring and the formation of $[Ru(\eta^4\text{-}C_5H_6)(\eta^6\text{-}C_6Ph_6)]$ (**14**) and $[Ru(\eta^4\text{-}C_5H_6)(\eta^6\text{-}C_6Ph_4Me_2)]$ (**15**). The reduction of (**9**) with Na–Hg in thf gives (**14**) and $[Ru(\eta^5\text{-}exo\text{-}C_6Ph_6H)(\eta\text{-}C_5H_5)]$.

In exploring the chemistry of transition-metal complexes containing four-electron donor alkyne ligands it was observed[2,3] that reaction of $Ag[BF_4]$ with $[Mo_2(CO)_6(\eta\text{-}C_5H_5)_2]$ and alkynes in dichloromethane as solvent leads to a redox reaction and the formation in high yield of the cations $[Mo(CO)(\eta^2\text{-}RC_2R')_2(\eta\text{-}C_5H_5)][BF_4]$ (R = R′ = alkyl or aryl). Subsequent studies showed that these cations provided a versatile entry point to the chemistry of molybdenum to carbon multiple bonded species.[4] In view of these observations we examined the related redox chemistry of $[Ru_2(CO)_4(\eta\text{-}C_5H_5)_2]$ in the belief that this might provide a synthetic pathway to ruthenium carbyne complexes. However, in the event[5] a different type of reaction occurs leading to the formation of a cationic η^4-cyclobutadiene complex.

Results and Discussion

Addition of $Ag[BF_4]$ to a stirred solution of $[Ru_2(CO)_4(\eta\text{-}C_5H_5)_2]$ and diphenylacetylene in CH_2Cl_2 afforded a silver mirror and the cationic yellow complex (**1**). Examination of the i.r. spectrum of (**1**) revealed the presence of a single terminal carbonyl band at 2 040 cm^{-1}. Elemental analysis and ^1H n.m.r. spectroscopy indicated that the molecular formula of (**1**) was $[Ru(CO)(PhC_2Ph)_2(\eta\text{-}C_5H_5)][BF_4]$; however, whilst the $^{13}C\text{-}\{^1H\}$ spectrum showed signals corresponding to CO and $\eta\text{-}C_5H_5$ ligands, resonances consistent with the presence of co-ordinated diphenylacetylene ligands were absent. In attempting to understand the nature of (**1**) the lability of the carbonyl ligand was next examined. In refluxing MeCN no reaction occurred; however, u.v. irradiation of a solution of (**1**) in MeCN led to the loss of CO and the formation in good yield of the purple crystalline complex (**2**). Analysis and the ^1H and $^{13}C\text{-}\{^1H\}$ n.m.r. spectra of (**2**) indicated that the simple replacement of the CO by co-ordinated MeCN had occurred. The relationship between (**1**) and (**2**) was further confirmed when it was found that (**2**) reacted with CO (10 atm/50 °C) in CH_2Cl_2 to form (**1**) in excellent yield.

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* Acetonitrile(η^5-cyclopentadienyl)(η^4-tetraphenylcyclobutadiene)ruthenium(II) tetrafluoroborate and (η^5-cyclopentadienyl)(η^4-1,2,3,4-tetraphenylbuta-1,3-dien-1-olato-C^{1-4},*O*)ruthenium(II) respectively.

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1987, Issue 1, pp. xvii—xx.

Non-S.I. unit employed: atm = 101 325 Pa.

Table 1. Selected bond lengths (Å) and interbond angles (°) for complex (**2**)

Ru–C(1)	2.192(2)	Ru–C(2)	2.208(3)	C(3)–C(4)	1.457(3)	C(31)–C(32)	1.396(4)
Ru–C(3)	2.177(2)	Ru–C(4)	2.175(2)	C(31)–C(36)	1.401(4)	C(4)–C(41)	1.481(3)
Ru–C(51)	2.191(3)	Ru–C(52)	2.255(3)	C(41)–C(42)	1.409(3)	C(41)–C(46)	1.393(4)
Ru–C(53)	2.237(3)	Ru–C(54)	2.234(3)	C(51)–C(52)	1.433(4)	C(51)–C(55)	1.426(4)
Ru–C(55)	2.246(3)	Ru–N	2.070(2)	C(52)–C(53)	1.396(4)	C(53)–C(54)	1.446(5)
C(1)–C(11)	1.475(3)	C(1)–C(2)	1.438(3)	C(54)–C(55)	1.391(5)	C(6)–C(7)	1.461(4)
C(1)–C(4)	1.497(3)	C(11)–C(12)	1.397(3)	C(6)–N	1.135(4)	F(1)–B	1.369(4)
C(11)–C(16)	1.400(3)	C(2)–C(21)	1.480(3)	F(2)–B	1.416(6)	F(3)–B	1.365(6)
C(2)–C(3)	1.486(3)	C(21)–C(22)	1.401(4)	F(4)–B	1.347(5)	F(5)–B	1.264(14)
C(21)–C(26)	1.393(4)	C(3)–C(31)	1.476(3)	F(6)–B	1.422(13)	F(7)–B	1.386(19)

C(1)–Ru–C(2)	38.2(1)	C(1)–Ru–C(3)	56.4(1)	C(2)–C(1)–C(4)	90.8(2)	Ru–C(2)–C(1)	70.3(1)
C(2)–Ru–C(3)	39.6(1)	C(1)–Ru–C(4)	40.1(1)	Ru–C(2)–C(21)	130.6(2)	C(1)–C(2)–C(21)	132.8(2)
C(2)–Ru–C(4)	57.0(1)	C(3)–Ru–C(4)	39.1(1)	Ru–C(2)–C(3)	69.1(1)	C(1)–C(2)–C(3)	89.9(2)
C(1)–Ru–C(51)	133.5(1)	C(2)–Ru–C(51)	95.3(1)	C(21)–C(2)–C(3)	135.2(2)	Ru–C(3)–C(2)	71.3(1)
C(3)–Ru–C(51)	88.9(1)	C(4)–Ru–C(51)	126.0(1)	Ru–C(3)–C(31)	126.6(2)	C(2)–C(3)–C(31)	132.0(2)
C(1)–Ru–C(52)	157.7(1)	C(2)–Ru–C(52)	126.6(1)	Ru–C(3)–C(4)	70.4(1)	C(2)–C(3)–C(4)	90.5(2)
C(3)–Ru–C(52)	101.4(1)	C(4)–Ru–C(52)	121.7(1)	C(31)–C(3)–C(4)	136.1(2)	Ru–C(4)–C(1)	70.6(1)
C(1)–Ru–C(53)	164.2(1)	C(2)–Ru–C(53)	156.3(1)	Ru–C(4)–C(3)	70.5(1)	C(1)–C(4)–C(3)	88.8(2)
C(3)–Ru–C(53)	136.8(1)	C(4)–Ru–C(53)	140.3(1)	Ru–C(4)–C(41)	131.6(2)	C(1)–C(4)–C(41)	133.6(2)
C(1)–Ru–C(54)	138.4(1)	C(2)–Ru–C(54)	128.1(1)	C(3)–C(4)–C(41)	134.3(2)	C(7)–C(6)–N	178.2(3)
C(3)–Ru–C(54)	149.1(1)	C(4)–Ru–C(54)	171.8(1)	C(6)–C(7)–H(71)	104.8(34)	C(6)–C(7)–H(72)	113.6(30)
C(1)–Ru–C(55)	125.7(1)	C(2)–Ru–C(55)	96.9(1)	H(71)–C(7)–H(72)	108.6(44)	C(6)–C(7)–H(73)	107.6(29)
C(3)–Ru–C(55)	113.8(1)	C(4)–Ru–C(55)	151.5(1)	H(71)–C(7)–H(73)	102.7(41)	H(72)–C(7)–H(73)	118.2(40)
C(1)–Ru–N	80.7(1)	C(2)–Ru–N	117.3(1)	Ru–N–C(6)	169.7(2)	F(1)–B–F(2)	105.6(3)
C(3)–Ru–N	126.6(1)	C(4)–Ru–N	87.7(1)	F(1)–B–F(3)	114.9(3)	F(2)–B–F(3)	105.8(3)
C(51)–Ru–N	143.4(1)	C(52)–Ru–N	115.8(1)	F(1)–B–F(4)	112.8(3)	F(2)–B–F(4)	106.2(4)
C(53)–Ru–N	83.5(1)	C(54)–Ru–N	84.2(1)	F(3)–B–F(4)	110.8(3)	F(1)–B–F(5)	119.4(8)
C(55)–Ru–N	117.0(1)	Ru–C(1)–C(11)	124.7(2)	F(1)–B–F(6)	93.5(6)	F(5)–B–F(6)	114.1(10)
Ru–C(1)–C(2)	71.5(1)	C(11)–C(1)–C(2)	133.4(2)	F(1)–B–F(7)	99.5(8)	F(5)–B–F(7)	118.6(12)
Ru–C(1)–C(4)	69.4(1)	C(11)–C(1)–C(4)	135.1(2)	F(6)–B–F(7)	108.2(10)		

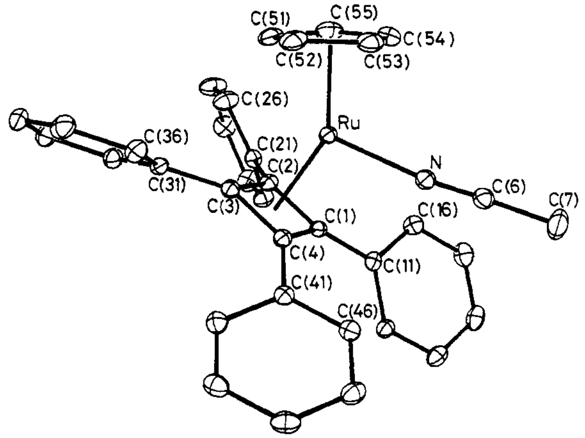
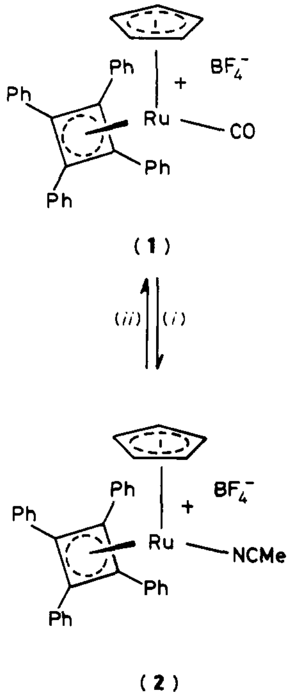


Figure 1. Molecular structure of the cation of (**2**). All hydrogen atoms have been omitted for clarity; ellipsoids have been drawn to enclose 30% probability density

There remained the problem as to how the two diphenylacetylene ligands were bonded to the ruthenium. This was elucidated by single-crystal *X*-ray crystallography, which established for the acetonitrile complex (**2**) the structure illustrated in Figure 1, selected bond lengths and interbond angles being listed in Table 1. The cation contains a ruthenium atom co-ordinated by η^5-cyclopentadienyl, η^4-tetraphenylcyclobutadiene, and acetonitrile. The η^4-C_4Ph_4 ligand, formally derived from two diphenylacetylene ligands, shows small but significant asymmetry in the Ru–C distances [2.192(2), 2.208(3), 2.177(2), and 2.175(2) Å for Ru–C(1),C(2),C(3),C(4) respectively]. This corresponds to a 'slip' of the ruthenium across the face of the η^4-C_4Ph_4 ring of 0.030 Å. The phenyl rings lie canted to the plane of the η^4-C_4Ph_4 ring so as to form a four-blade propeller with interplanar angles 40.0, 43.1, 33.9, and 32.3° for the rings on C(1), C(2), C(3), and C(4) respectively. In each case the *ipso* carbon of the phenyl lies out of the C(1—4) plane on the opposite side to the ruthenium atom [deviations are 0.157, 0.291, 0.222, 0.356, and -1.925 Å for C(11), C(21), C(31), C(41), and Ru respectively]. The orientation of the η^4-C_4Ph_4 ligand has the C(1)–C(2) and C(3)–C(4) bonds near parallel to the plane defined by the ruthenium atom and the centroids of the η^4-C_4Ph_4 and η-C_5H_5 rings (deviating by 6.5 and 7.0° respectively). The cyclobutadiene ring is markedly rectangular with C(1)–C(2) and C(3)–C(4) long and C(1)–C(4) and C(2)–C(3) short (see Table 1). We have shown[5] that this distortion may be related to the effect of the frontier orbitals of the d^6 $RuL(\eta\text{-}C_5H_5)^+$ fragment on the relative occupancies of the two components of the e_g set of cyclobutadiene π orbitals. The lower symmetry of the cation of (**2**) (approx. C_s) and of the $Ru(NCMe)(\eta\text{-}C_5H_5)^+$ moiety is reflected in the rectangular distortion of the ring. The C–C distances within the η-C_5H_5 ring also show significant distortions away from the highest possible symmetry (D_{5h}), such that C(54)–C(55) and C(52)–C(53) are short and the other C–C long (see Table 1). This in turn may be rationalised as a consequence of the perturbation of the e''_1 orbital occupancies of $C_5H_5^-$ by the $Ru(\eta^4\text{-}C_4Ph_4)L^{2+}$ moiety. We note that the cation of (**2**) may be viewed as an opened sandwich structure with the acetonitrile ligand lying in the plane between the η^4-C_4Ph_4 and η-C_5H_5 ligands; the angle between the η-C_5H_5 and η^4-C_4Ph_4 ring planes is 145.8°.

Thus, these observations firmly established the structural relationships illustrated in Scheme 1; however, the important question remained as to the origin of the η^4-tetraphenylcyclobutadiene ligand. In carrying out the reaction which affords (**1**), the alkyne complex $[Ru(CO)_2(\eta^2\text{-}PhC_2Ph)(\eta\text{-}C_5H_5)][BF_4]$ (**3**) was occasionally isolated in low yield together with $[Ru(CO)_3(\eta\text{-}C_5H_5)][BF_4]$. Clearly (**3**) was a possible precursor



Scheme 1. (*i*) MeCN, u.v. irradiation; (*ii*) CO (10 atm/50 °C), CH_2Cl_2

of the η^4-cyclobutadiene cation of (**1**), and it was found that (**3**) could alternatively be formed in high yield by a straightforward adaptation of the procedure of Reger *et al.*[6] for the synthesis of the iron analogue. Attempts, however, to form (**1**) from (**3**) by a thermal reaction with diphenylacetylene were unsuccessful, implying that a more complex reaction sequence was involved.

There are two other possible pathways to (**1**). One involves abstraction of CO from (**3**) by the 16-electron cation of $[Ru(CO)_2(\eta\text{-}C_5H_5)][BF_4]$, which is probably formed on oxidative cleavage of $[Ru_2(CO)_4(\eta\text{-}C_5H_5)_2]$. This could lead to the formation of the species $[Ru(CO)(\eta^2\text{-}PhC_2Ph)(\eta\text{-}C_5H_5)]^+$, a possible precursor of (**1**). However, attempts to reproduce this reaction sequence proved unsuccessful; generation of the 16-electron cation $[Ru(CO)_2(\eta\text{-}C_5H_5)]^+$ (ν_{CO} at 2 058, 2 021 cm^{-1}) by cleavage of $[Ru_2(CO)_4(\eta\text{-}C_5H_5)_2]$ with $Ag[BF_4]$ {or by halide abstraction from $[RuBr(CO)_2(\eta\text{-}C_5H_5)]$} in the presence of (**3**) did not produce either $[Ru(CO)_3(\eta\text{-}C_5H_5)][BF_4]$ or $[Ru(CO)(\eta^2\text{-}PhC_2Ph)(\eta\text{-}C_5H_5)][BF_4]$. An alternative route to (**1**) involves disproportionation of the initially formed cation $[Ru(CO)_2(\eta\text{-}C_5H_5)]^\bullet$ to give $[Ru(CO)_3(\eta\text{-}C_5H_5)]^+$ and the 14-electron cation $[Ru(CO)(\eta\text{-}C_5H_5)]^+$, which is then captured by PhC_2Ph resulting in the formation of (**1**). This idea derives support from the observation that dichloromethane solutions of $[Ru(CO)_2(\eta\text{-}C_5H_5)][BF_4]$ decompose slowly under a nitrogen atmosphere affording $[Ru(CO)_3(\eta\text{-}C_5H_5)][BF_4]$ and an unidentified brown solid, a result paralleled in the analogous iron system.[6] Additionally it is of note that this reaction pathway requires that the yield of (**1**) does not exceed 50%, a fact in agreement with the experimental yields of 35—42%.

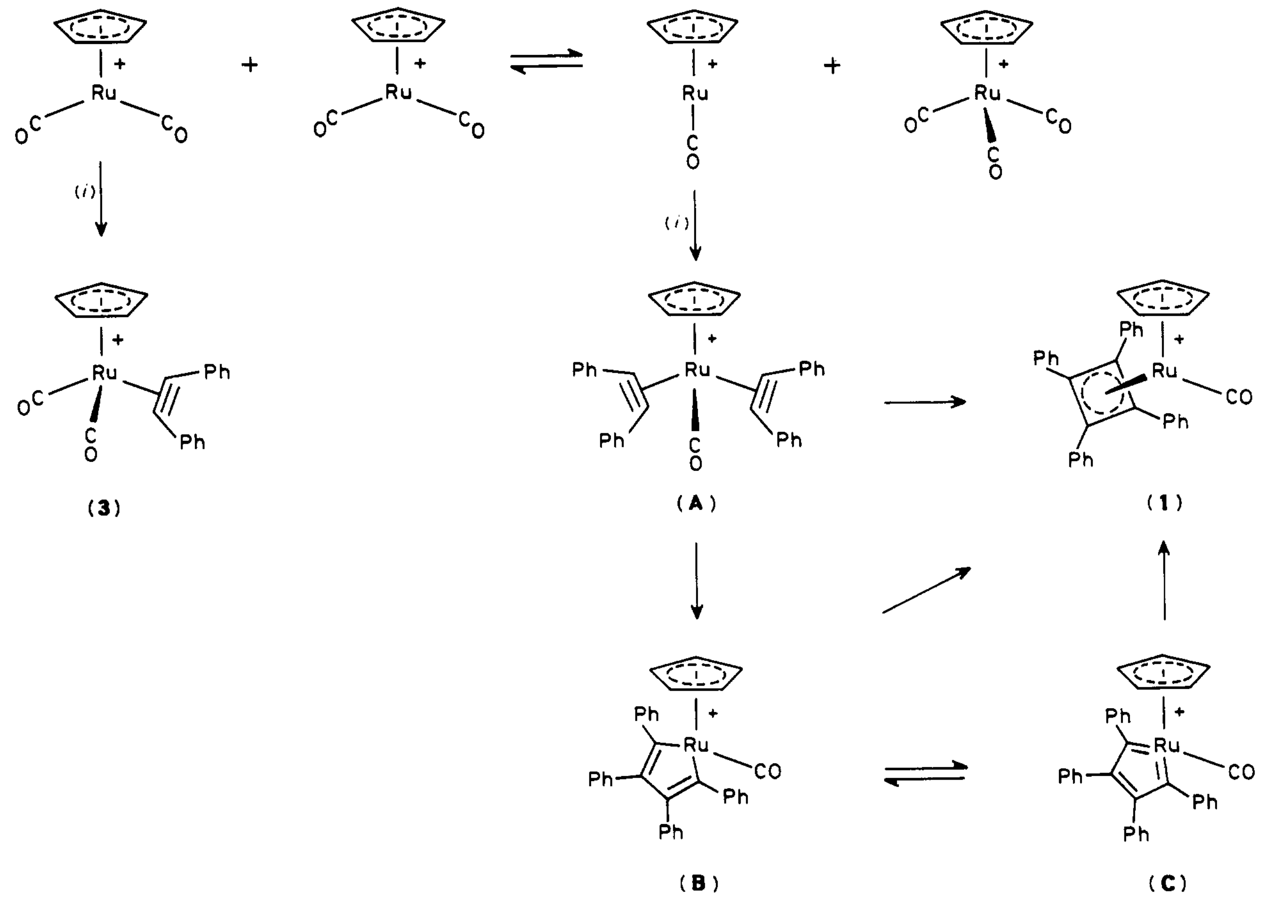
These possible pathways to (**1**) are summarised in Scheme 2. There remains the important question as to how the two diphenylacetylene ligands couple to form the η^4-C_4Ph_4 ring. Recent[7,8] flash-thermolysis experiments with η^4-cyclobutadiene(η-cyclopentadienyl)cobalt complexes have been interpreted in terms of the equilibrium process $[Co(\eta^4\text{-}C_4R_4)(\eta\text{-}C_5H_5)] \rightleftharpoons [Co(\eta^2\text{-}RC_2R)_2(\eta\text{-}C_5H_5)]$ implying that a possible pathway to (**1**) is *via* the intermediate (**A**) (Scheme 2). Alternatively, oxidative coupling of the two alkynes to form a 16-electron ruthena(IV)cyclopentadiene (**B**) is a second possibility; (**B**) then undergoes either a reductive elimination to give (**1**) or an electronic rearrangement to form a ruthena(VI)cyclopentatriene[9] (**C**), which collapses to (**1**). At present it is not possible to distinguish between these possibilities.

From a synthetic standpoint these reactions provide access to cationic η^4-cyclobutadiene complexes. This type of complex has been previously prepared by (*i*) halide abstraction,[10,11] (*ii*) nitrosylation of neutral carbonyl-substituted complexes,[12,13] (*iii*) reaction of but-2-yne with *trans*-$[Pt(CF_3)(PMe_2Ph)_2(Me_2CO)][PF_6]$,[14] (*iv*) alkylation of η^3-cyclobutenonylcobalt(I) complexes,[15,16] and (*v*) by one-electron oxidation of metal–cyclobutadiene complexes[17,18] but their chemistry has not been exploited. It was, therefore, important to begin to examine the reaction chemistry of (**1**) and (**2**).

As previously described, (**1**) does not react thermally with MeCN; however, u.v. irradiation affords the acetonitrile complex (**2**) (Scheme 1), presumably *via* photodissociation of CO to form the 16-electron cation $[Ru(\eta^4\text{-}C_4Ph_4)(\eta\text{-}C_5H_5)][BF_4]$, which is captured by MeCN. Similarly, (**1**) is thermally unreactive towards $[NMe_4]Br$ in dichloromethane; however, u.v. irradiation of the reaction mixture led to a progressive decrease in the intensity of the carbonyl stretching band due to (**1**). On completion of the reaction, addition of diethyl ether afforded black crystals of (**4**) (Scheme 3). This neutral complex was also formed in good yield on reaction of the labile acetonitrile complex (**2**) with $[NMe_4]Br$ in CH_2Cl_2, and in a similar way the corresponding chloro complex (**5**) could be prepared. Elemental analysis, ^1H and $^{13}C\text{-}\{^1H\}$ n.m.r. (see Experimental section) suggested that these complexes contained intact η^4-C_4Ph_4 ligands, a view which was reinforced by the observation that addition of $Ag[BF_4]$ to a solution of (**5**) in MeCN afforded AgCl and (**2**). There was, however, an alternative bonding mode for (**4**) and (**5**) which was suggested by the recent observation[9] that $[RuCl(\eta^4\text{-cod})(\eta\text{-}C_5H_5)]$ (cod = cyclo-octa-1,5-diene) reacts with PhC_2H to form $[RuCl\{\sigma,\sigma'\text{-}C_4Ph_2H_2\}(\eta\text{-}C_5H_5)]$ a ruthena(VI)cyclopentatriene, characterised by *X*-ray crystallography. The ^{13}C n.m.r. spectrum of this compound showed a low-field resonance characteristic of a carbon atom doubly bonded to ruthenium. There was no evidence, however, in the ^{13}C spectra of (**4**) and (**5**) for low-field contact carbon resonances, supporting the view that these complexes had not undergone a C_4 ring-opening reaction to form $[RuX\{\sigma,\sigma\text{-}C_4Ph_4\}(\eta\text{-}C_5H_5)]$, a structural analogue of the complex prepared by Singleton and co-workers.[9] In this context it is interesting that (**4**) was unaffected by u.v. irradiation, showing no tendency to undergo an η^4(4 e) to σ,σ'(4 e) transformation of the bonding mode of the C_4Ph_4 ligand.

The thiolate anion of $Na[SC_6H_4Me\text{-}4]$ also reacts with (**2**). In dichloromethane as solvent, a colour change occurred at room temperature forming two complexes, (**6**) and (**7**), which were separated by column chromatography. Elemental analysis, mass spectroscopy, ^1H and ^{13}C n.m.r. spectroscopy showed that the red complex (**6**) was $[Ru(SC_6H_4Me\text{-}4)(\eta^4\text{-}C_4Ph_4)(\eta\text{-}C_5H_5)]$, a structural analogue of the halogeno complexes (**4**) and (**5**). The second product of this reaction, the golden yellow crystalline complex (**7**) could not, however, be identified by spectroscopic techniques, and therefore a single-crystal *X*-ray diffraction study was undertaken. This established the structure shown in Figure 2, selected bond lengths and angles being listed in Table 2.

The ruthenium atom is co-ordinated to an η^5-cyclopentadienyl ligand and an η^5(5 e)-bonded butadienolato fragment with the oxygen atom occupying a terminal position. The terminal carbon atom, C(4), of the butadienolate is bonded to a phenyl group and a hydrogen atom with the hydrogen in an *anti* (inside) position. The Ru–C bond lengths are 2.210(5), 2.190(5), 2.167(5), and 2.228(5) Å for C(1), C(2), C(3), and C(4) respectively. The Ru–O(1) bond length is 2.127(3) Å. The C_4O

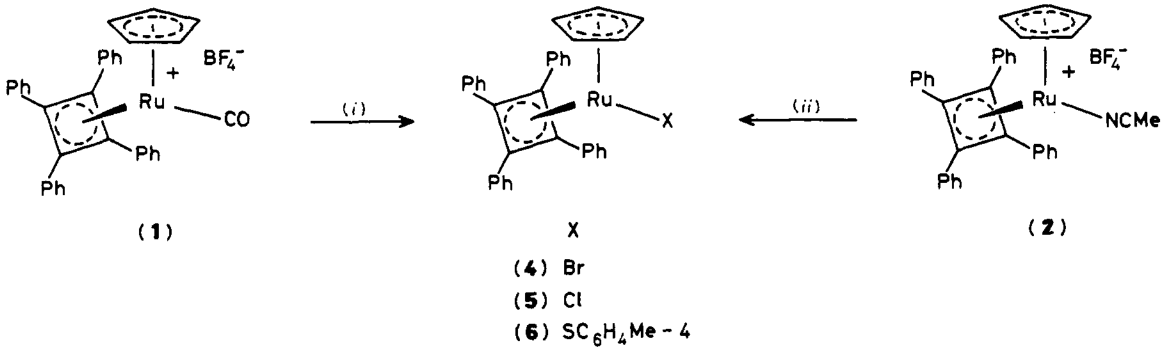


Scheme 2. Counter anion BF_4^-. (*i*) $+PhC_2Ph$, CH_2Cl_2

Table 2. Selected bond lengths (Å) and interbond angles (°) for complex (7)

Ru–C(1)	2.210(5)	Ru–C(2)	2.190(5)	C(1)–O(1)	1.296(6)	C(2)–C(3)	1.464(7)
Ru–C(3)	2.167(5)	Ru–C(4)	2.228(5)	C(2)–C(26)	1.503(6)	C(3)–C(4)	1.423(7)
Ru–C(50)	2.163(6)	Ru–C(51)	2.150(7)	C(3)–C(36)	1.511(6)	C(4)–C(46)	1.491(7)
Ru–C(52)	2.191(7)	Ru–C(53)	2.206(6)	C(50)–C(51)	1.418(10)	C(50)–C(54)	1.398(8)
Ru–C(54)	2.204(6)	Ru–O(1)	2.127(3)	C(51)–C(52)	1.393(9)	C(52)–C(53)	1.404(10)
C(1)–C(2)	1.455(7)	C(1)–C(16)	1.495(6)	C(53)–C(54)	1.405(10)		
C(1)–Ru–C(3)	71.3(2)	C(1)–Ru–C(2)	38.6(2)	C(4)–Ru–O(1)	74.0(2)	C(3)–Ru–O(1)	85.2(2)
C(1)–Ru–C(4)	82.7(2)	C(2)–Ru–C(3)	39.3(2)	C(51)–Ru–O(1)	162.2(2)	C(50)–Ru–O(1)	148.6(2)
C(3)–Ru–C(4)	37.7(2)	C(2)–Ru–C(4)	68.7(2)	C(53)–Ru–O(1)	104.5(2)	C(52)–Ru–O(1)	124.9(2)
C(2)–Ru–C(50)	111.6(2)	C(1)–Ru–C(50)	126.2(2)	Ru–C(1)–C(2)	69.9(3)	C(54)–Ru–O(1)	114.7(2)
C(4)–Ru–C(50)	136.5(2)	C(3)–Ru–C(50)	114.6(2)	C(2)–C(1)–C(16)	123.0(4)	Ru–C(1)–C(16)	136.5(3)
C(2)–Ru–C(51)	129.5(2)	C(1)–Ru–C(51)	162.4(2)	C(2)–C(1)–O(1)	121.4(4)	Ru–C(1)–O(1)	69.1(3)
C(4)–Ru–C(51)	105.6(2)	C(3)–Ru–C(51)	105.6(2)	Ru–C(2)–C(1)	71.4(3)	C(16)–C(1)–O(1)	115.5(4)
C(2)–Ru–C(52)	164.9(2)	C(1)–Ru–C(52)	156.3(2)	C(1)–C(2)–C(3)	121.7(4)	Ru–C(2)–C(3)	69.5(3)
C(4)–Ru–C(52)	104.9(2)	C(3)–Ru–C(52)	128.0(2)	C(1)–C(2)–C(26)	118.9(4)	Ru–C(2)–C(26)	130.0(3)
C(2)–Ru–C(53)	155.1(2)	C(1)–Ru–C(53)	122.9(2)	Ru–C(3)–C(2)	71.2(3)	C(3)–C(2)–C(26)	119.3(4)
C(4)–Ru–C(53)	133.7(2)	C(3)–Ru–C(53)	165.2(2)	C(2)–C(3)–C(4)	119.4(4)	Ru–C(3)–C(4)	73.5(3)
C(2)–Ru–C(54)	122.7(2)	C(1)–Ru–C(54)	109.9(2)	C(2)–C(3)–C(36)	119.3(4)	Ru–C(3)–C(36)	126.1(3)
C(4)–Ru–C(54)	167.2(2)	C(3)–Ru–C(54)	147.6(2)	Ru–C(4)–C(3)	68.8(3)	C(4)–C(3)–C(36)	121.3(4)
C(2)–Ru–O(1)	67.6(2)	C(1)–Ru–O(1)	34.7(2)	C(3)–C(4)–C(46)	128.2(4)	Ru–C(4)–C(46)	125.6(3)
						Ru–O(1)–C(1)	76.2(3)

chain is essentially planar, deviations from the mean plane being 0.042, −0.036, −0.014, 0.053, and −0.045 Å and with torsion angles C(1)C(2)C(3)C(4) of 6.7(7)° and O(1)C(1)C(2)C(3) of 1.9(6)°. The internal angles of the C_4O chain are 121.4(4), 121.7(4), and 119.4(4)°, *i.e.* these five atoms give vertices of a distorted hexagon. The planes of the butadienolato and cyclopentadienyl ligands are very nearly parallel (interplanar angle = 6.5°), thus the molecule may be thought of as an analogue of ruthenocene. The phenyl rings attached to the butadienolato ligand are canted to the C_4O plane making



Scheme 3. (*i*) [NMe_4]X, u.v. irradiation; (*ii*) [NMe_4]X, CH_2Cl_2

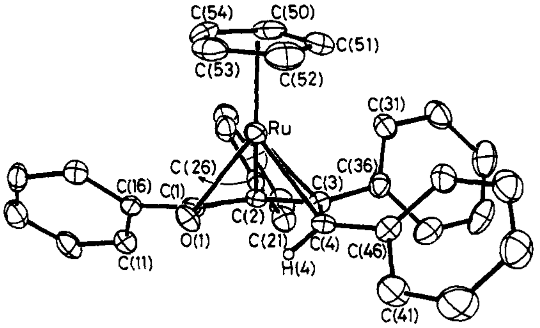
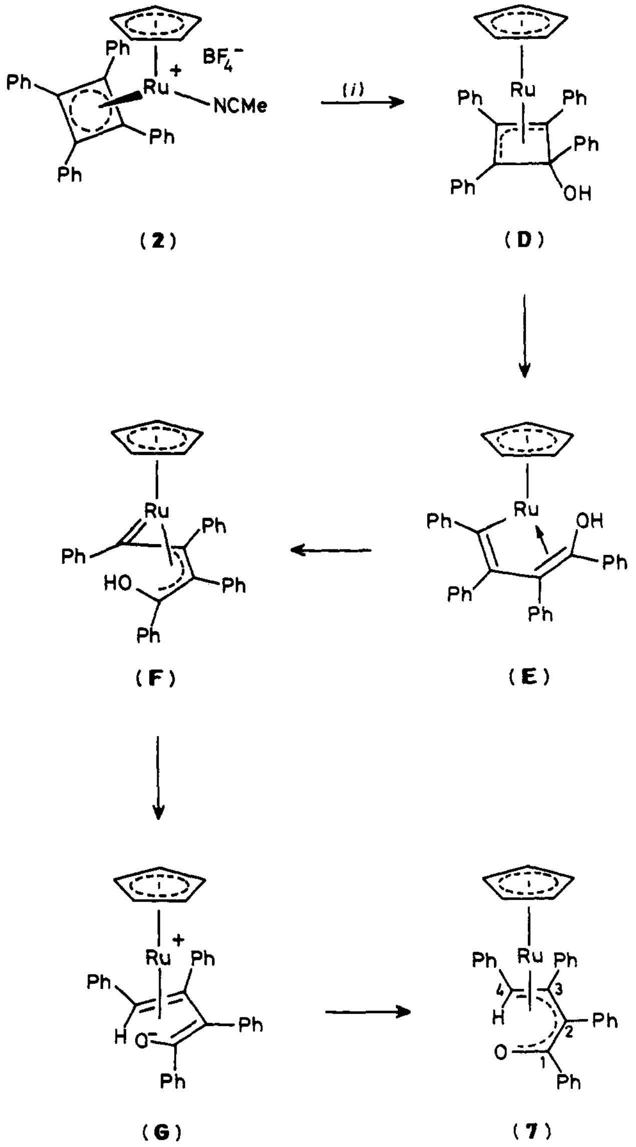


Figure 2. Molecular structure of (7). All phenyl and cyclopentadienyl group hydrogen atoms have been omitted for clarity; ellipsoids have been drawn to enclose 30% probability density

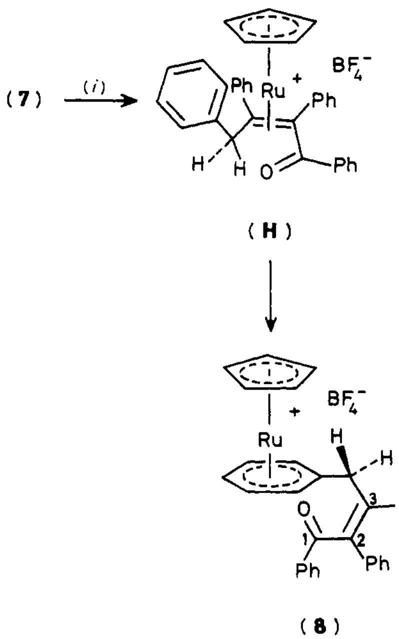
angles of 49.7, 58.1, 57.4, and 49.5° for those phenyl groups on C(1), C(2), C(3), and C(4) respectively. The *ipso* carbons of these groups lie on the same side of the C_4O plane as ruthenium except for C(16); deviations are −0.172, 0.027, 0.247, and 0.085 Å for C(16), C(26), C(36), and C(46) respectively. The hydrogen atom H(4) lies markedly out of plane (−0.53 Å) away from the ruthenium. The C(3)–C(4) distance is noticeably shorter than C(2)–C(3) and C(1)–C(2).

Thus it is clear that the η^4-C_4Ph_4 ring present in (**2**) has undergone a ring-opening reaction, presumably triggered by nucleophilic attack of a hydroxide anion, which is generated by the presence of water in the Na[SC_6H_4Me-4]. In agreement with this hypothesis, addition of a small amount of water greatly improved the yield of (**7**). Of the three possible sites presented by the cation of (**2**) for attack by a hydroxide ion the formation of (**7**) can be most easily understood if the nucleophile approaches a carbon atom of the η^4-C_4Ph_4 ring from the opposite face to which the ruthenium is bonded. As is shown in Scheme 4 such a reaction would lead to the formation of the η^3-cyclobutenyl complex (**D**), which can then undergo a conrotatory ring-opening reaction to form the σ,η^2(3 e)-butadienyl species (**E**) carrying a hydroxyl group on the 'inside' position. We have previously suggested[19] that a 16-electron σ,η^2(3 e)-butadienyl species of this type can undergo an electronic and geometric rearrangement to form an 18-electron σ,η^3(5 e)-butadienyl complex. An extension of this idea suggests that (**E**) would rearrange into (**F**). Such a species could then form (**7**) simply by undergoing an intramolecular protolysis of the C^α (alkylidene) carbon[20] followed by an electronic reorganisation.

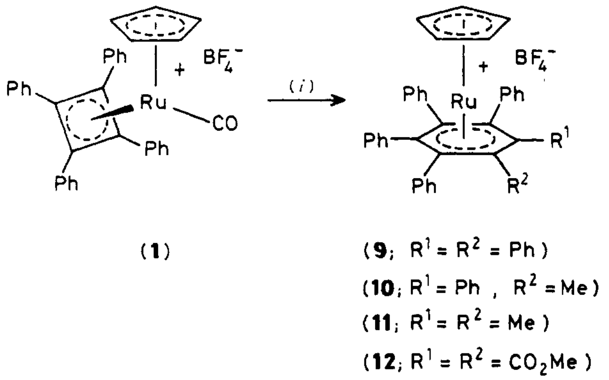


Scheme 4. (*i*) H_2O–NaOH

With the identity of (**7**) established it was interesting to begin to explore its reactivity. Addition of $HBF_4 \cdot Et_2O$ at low temperature to a dichloromethane solution of (**7**) led on warm-up to a colour change and the formation of the cationic species (**8**). Elemental analysis indicated that a simple protolysis reaction had occurred and this was confirmed by examination of the ^1H and ^{13}C-{^1H} n.m.r. spectra, which showed features (see Experimental section) characteristic of an arene(cyclo-



Scheme 5. (*i*) $HBF_4 \cdot Et_2O$, CH_2Cl_2



Scheme 6. (*i*) $+R^1C_2R^2$, u.v. irradiation

pentadienyl)ruthenium cation. This implies that protonation leads either directly or indirectly to the co-ordinatively unsaturated cation (**H**) in Scheme 5, which stabilises itself by initial co-ordination of the benzyl arene ring followed by complete slippage to form the η^6-bonded arene cation of (**8**).

An alternative and more versatile synthetic pathway to arene(η-cyclopentadienyl)ruthenium cations was discovered when the reactions of $[Ru(CO)_2(\eta^2\text{-}PhC_2Ph)(\eta\text{-}C_5H_5)][BF_4]$ (**3**) and (**1**) with diphenylacetylene were explored. As previously mentioned (**3**) does not react thermally with PhC_2Ph; however, u.v. irradiation in CH_2Cl_2 solution led to the slow (52 h) disappearance (i.r.) of the starting material, and when diethyl ether was added to the reaction mixture a low yield (12%) of the white crystalline complex (**9**) was obtained. This same complex was obtained in much higher yield (76%), and with shorter reaction times (6 h) by u.v. irradiation of (**1**) and PhC_2Ph in CH_2Cl_2.

The i.r. spectrum of (**9**) showed no carbonyl bands and when the ^1H and $^{13}C\text{-}\{^1H\}$ n.m.r. spectra (see Experimental section) were considered in the light of the analytical data it was clear that (**9**) had the structure illustrated in Scheme 6. The photochemical reaction of (**1**) with alkynes proved to be general, the corresponding reactions with PhC_2Me, MeC_2Me, and $MeO_2CC_2CO_2Me$ affording the sterically crowded arene cations (**10**), (**11**), and (**12**) respectively. In each case the product was isolated in good yield as an air-stable white or cream crystalline solid, identified by elemental analysis and ^1H and $^{13}C\text{-}\{^1H\}$ n.m.r. spectroscopy.

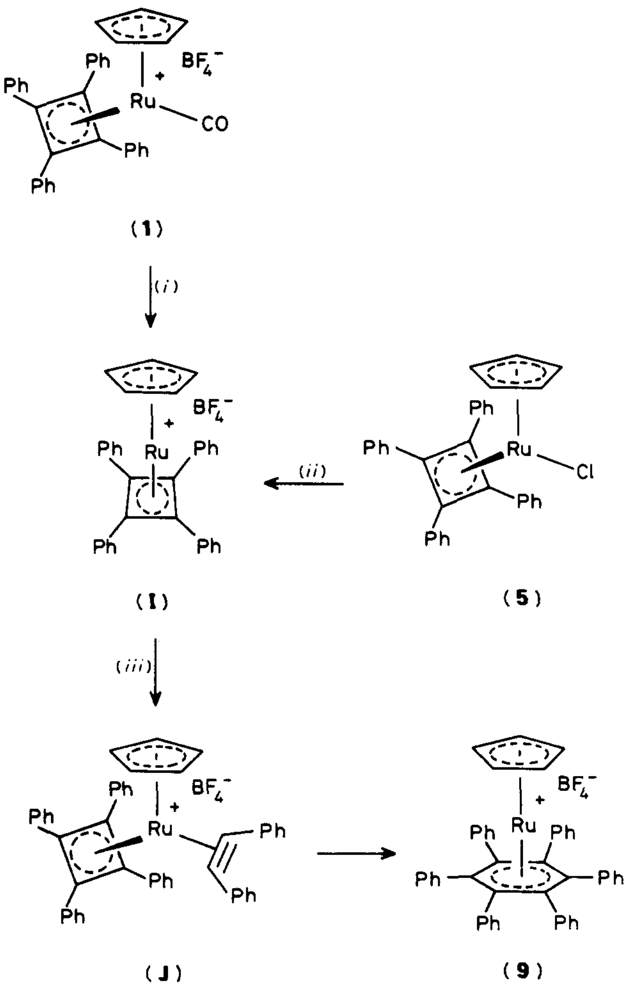
Prior to this work a number of ruthenium arene cations have been synthesised, mainly either by reaction of $[\{RuCl_2(\eta^6\text{-}arene)\}_n]$ with TlC_5H_5,[21] or by high-temperature $AlCl_3$–Al catalysed reactions of ruthenocene with arenes.[22] More recently[23] the reaction of $[RuCl(\eta^3\text{-}C_3H_5)(\eta^6\text{-}C_6H_6)]$ with diphenylacetylene in the presence of $Ag[BF_4]$ has been reported to afford $[Ru(\eta^5\text{-}C_5H_3Ph_2)(\eta^6\text{-}C_6H_6)][BF_4]$.

Although early on in the development of organometallic chemistry the idea was proposed[24] that η^4-cyclobutadiene complexes could act as relay points on the path from alkynes to arenes, this was not supported by a study[25] of the cyclotrimerisation of $CD_3C{\equiv}CCH_3$ by a variety of transition-metal catalysts. As a result interest centred in the intervening years on alternative pathways from alkynes to arenes involving (*i*) addition of alkynes to metallacyclopentadienes,[26–29] (*ii*) concerted $(2 + 2 + 2)\pi$ cycloaddition reactions at a metal centre,[30] and (*iii*) the stepwise insertion of co-ordinated alkynes into metal—vinyl carbon bonds followed by a cyclisation step.[31] However, the observations summarised in Scheme 6 serve to refocus attention on reactive cyclobutadiene complexes as precursors of arenes.

Insight into this $C_4 + C_2 \longrightarrow C_6$ ring expansion reaction was provided by the observation that treatment of the chloro complex $[RuCl(\eta^4\text{-}C_4Ph_4)(\eta\text{-}C_5H_5)]$ (**5**) with $Ag[BF_4]$ and diphenylacetylene in dichloromethane as solvent gave AgCl and $[Ru(\eta^6\text{-}C_6Ph_6)(\eta\text{-}C_5H_5)][BF_4]$ (**9**) as products. Since reaction of (**5**) with $Ag[BF_4]$ in acetonitrile gives (**2**), this suggests that in the corresponding reaction with PhC_2Ph, the co-ordinatively unsaturated cation $[Ru(\eta^4\text{-}C_4Ph_4)(\eta\text{-}C_5H_5)]^+$ (**I**) is generated, which is then captured by a molecule of diphenylacetylene (Scheme 7). There are then a number of possible pathways from the adduct (**J**) to the arene cation (**9**), which cannot be distinguished between with the evidence presently available. These include (*i*) the intermediacy of a hexaphenylbicyclo[2.2.0]hexadiene complex, which is formed either directly from (**J**) or *via* a stepwise oxidation–reduction sequence, (*ii*) transformation of the η^4-cyclobutadiene into a ruthenacyclopentadiene followed either by a $(4 + 2)\pi$ addition of the co-ordinated alkyne or insertion of the alkyne and reductive elimination of the arene from a ruthenacycloheptatriene.

Attempts to generalise the synthetic route leading to the formation of (**1**) by the utilisation of other alkynes were unsuccessful. However, during the course of an investigation of the reaction between $[Ru_2(CO)_4(\eta\text{-}C_5H_5)_2]$, $Ag[BF_4]$, and EtC_2Et, it was found that repetition of the reaction in the presence of a nitrogen purge and an excess of the alkyne led to the formation of a previously unobserved product. Isolation of this material as a white solid in low yield (9%) permitted its characterisation as the sandwich cation $[Ru(\eta^6\text{-}C_6Et_6)(\eta\text{-}C_5H_5)][BF_4]$ (**13**), identified by elemental analysis and ^1H and $^{13}C\text{-}\{^1H\}$ n.m.r. spectroscopy. It is presumed that a similar sequence of reactions is involved in the formation of (**13**) as has been discussed for the other arene cations.

Recently[32] there has been considerable attention paid to the static and dynamic stereochemistries of both free hexaethylbenzene (C_6Et_6) and of $\eta^6\text{-}C_6Et_6$ metal complexes, and therefore the isolation of (**13**) was especially interesting. Mislow and co-workers[33–35] have shown that for tripodal $[ML_3(\eta^6\text{-}C_6Et_6)]$ (L = CO or phosphine) complexes there are four energetically favoured conformations for the $\eta^6\text{-}C_6Et_6$ ligand, and that these stereoisomers interconvert in solution by uncorrelated ethyl group rotation. However, lately[34,36,37] there has been some controversy arising from the interpretation of

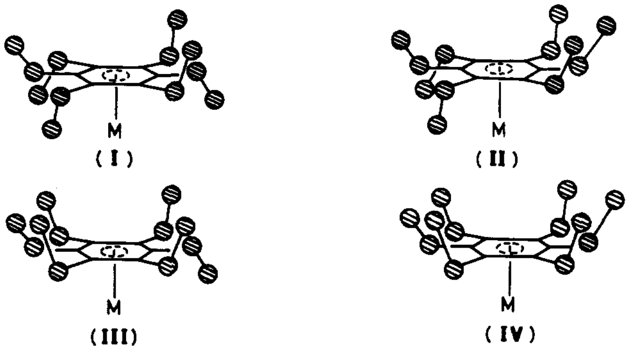


Scheme 7. (*i*) u.v.; (*ii*) Ag[BF_4], $-$AgCl; (*iii*) $+PhC_2Ph$

the corresponding n.m.r. spectra of the related complex [$Cr(CO)_2(CS)(\eta^6-C_6Et_6)$] and by implication those of [$M(CO)_3(\eta^6-C_6Et_6)$] in terms of rotation about the metal–arene bond.

Against this background an investigation of the stereodynamics of complex (**13**) appeared to be of value. The room-temperature ^1H n.m.r. spectrum of (**13**) shows resonances at δ 5.25 (s, 5 H, C_5H_5), 2.69 [q, 12 H, CH_2, *J*(HH) 7.4 Hz], and 1.34 [t, 18 H, Me, *J*(HH) 7.4 Hz], whilst the $^{13}C-\{^1H\}$ spectrum contains signals at δ 106.9 (C_6Et_6), 81.8 (C_5H_5), 23.1 (CH_2), and 17.4 p.p.m. (Me). Thus at ambient temperatures the ethyl groups of the C_6Et_6 ring are equivalent due to rapid ethyl group rotation about the ethyl–arene bond. However, the 200-MHz ^1H spectra recorded in the temperature range 218—193 K show a coalescence phenomenon, the triplet and quartet due to the methyl and methylene protons showing a loss of structure until eventually two broad singlets are obtained. At lower temperatures (193—183 K) these singlets begin to show some fine structure, although insufficient for diagnostic purposes.

The low-temperature 100.6-MHz $^{13}C-\{^1H\}$ spectrum of (**13**) in CD_2Cl_2–$CFCl_3$ was more informative. Although the η-C_5H_5 resonance is temperature invariant, the single contact arene ring resonance observed at room temperature collapses on cooling, so that at 183 K two singlets are observed at δ 106.1 and 102.1 p.p.m. ($\Delta G^{\ddagger}_{205}$ 39.2 ± 1.2 kJ mol^{-1}). The methyl and methylene signals exhibit corresponding behaviour, collapse to a doublet occurring in each case. On further cooling to 143 K the ethyl and arene signals sharpen considerably, suggesting that at very low temperatures only the most favoured distal stereoisomer (**I**) (Scheme 8) is present.



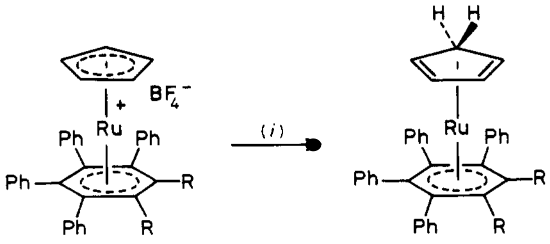
Scheme 8. Conformations of [$Ru(\eta^6-C_6Et_6)(\eta-C_5H_5)$][$BF_4$], M = $Ru(\eta-C_5H_5)^+BF_4^-$

The only other reported mixed C_5–C_6Et_6 sandwich complex is [$Fe(\eta^6-C_6Et_6)(\eta-C_5H_5)$][$PF_6$].[38] In contrast to (**13**), the low-temperature $^{13}C-\{^1H\}$ spectrum of the iron complex reveals the presence of three isomers in solution [isomers (**II**), (**III**), and (**IV**)], but not the 1,3,5-distal isomer (**I**) (Scheme 8).[35] In sandwich complexes of this type the conformation adopted by the C_6Et_6 ligand essentially represents a compromise between the minimalisation of steric interactions between vicinal ethyl groups, and between the ethyl groups and the cyclopentadienyl ring. Hence the difference in the favoured (lowest energy) stereoisomer of (**13**) and those of the iron analogue is most likely attributable to the greater size of the ruthenium atom.

Of particular note are the different linewidths seen for each of the resonances of the arene carbon subspectrum at a temperature within the range appropriate to intermediate rates of exchange, *i.e.* 183—163 K. These differing $T_c^{\ddagger}$ values imply the presence of other stereoisomers, and it is therefore probable that within this temperature range slowed ethyl group rotation occurs *via* the series of other stereoisomers whose populations are too low to be detectable.

In a mixed C_5–C_6 sandwich compound it is not required that the rings be parallel or that the principal rotational axis of the individual rings be coincident.[37] This observation stems from the fact that if, within such a molecule, the ring of higher rotational symmetry does not contain the rotational elements of the ring of low symmetry, the mixed sandwich complex consequently lacks overall rotational symmetry. Such is the case for (**13**). Indeed for (**13**) there are 15 equivalent major low-energy rotamers resulting from rotation of the C_5 and C_6 rings about the metal centre. Thus in the event that the rate for the relative rotation of the rings could be brought within the n.m.r. time-scale, subspectra consistent with C_5 symmetry would be observed for the cyclopentadienyl, arene, and ethyl carbons. Such is not the case and it is therefore apparent that, as for [$Fe(\eta^6-C_6Et_6)(\eta-C_5H_5)$][$PF_6$], cyclic moiety rotation about the metal remains rapid down to 143 K.

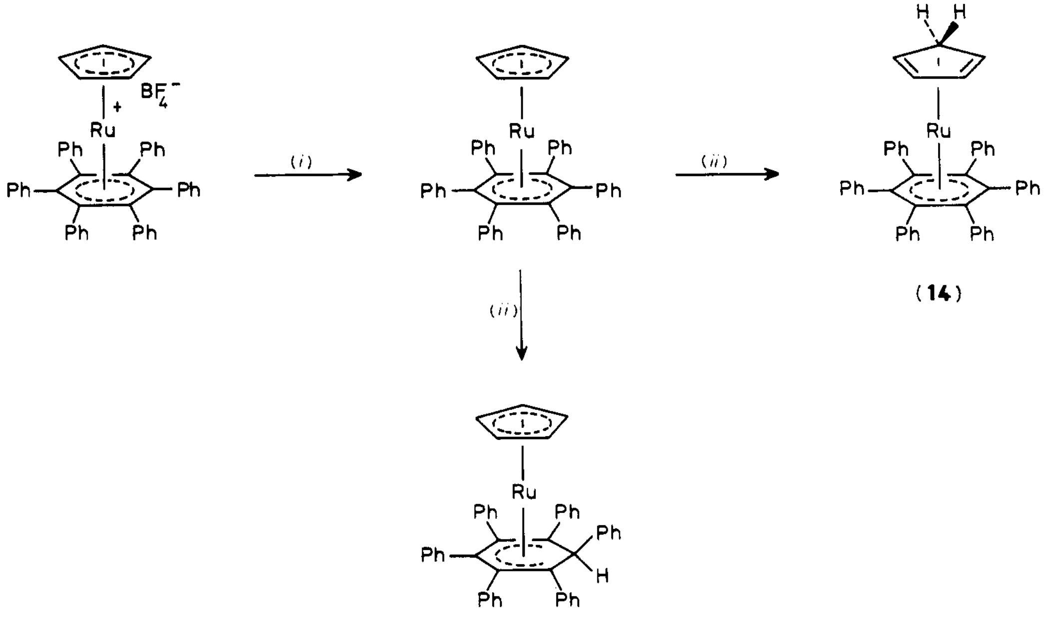
Whilst the chemistry of cationic iron complexes of the type [$Fe(\eta^6$-arene$)(\eta-C_5H_5)]^+$ has been studied in some detail, relatively little is known about the corresponding ruthenium and osmium systems. Indeed studies on the chemistry of such cations have largely been confined to a report by Stephenson *et al.*[21] describing the synthesis of the cations [$M(\eta^6$-arene)-$(\eta-C_5H_5)]^+$ (M = Ru, arene = C_6H_6, *p*-$MeC_6H_4CHMe_2$, $C_6H_5(OMe)$, or C_6Me_6; M = Os, arene = C_6H_6 or *p*-$MeC_6H_4CHMe_2$) and their reactivity towards nucleophiles.



(**9**; R = Ph) (**14**; R = Ph)

(**11**; R = Me) (**15**; R = Me)

Scheme 9. (*i*) $\mathrm{K[BHBu^s_3]}$, thf



(**14**)

(**16**)

Scheme 10. (*i*) Na–Hg, thf; (*ii*) H• abstraction from thf

Out of this study arose the observation that the above complexes either showed no reactivity towards nucleophiles (M = Ru, nucleophile = PR_3; M = Os, nucleophile = PR_3, H^-, CN^-, or OH^-) or reacted with extensive decomposition (M = Ru, nucleophile = CN^- or OH^-). In only one instance was nucleophilic attack on the arene ring observed, $[\mathrm{Ru}(\eta^6\text{-}C_6H_6)(\eta\text{-}C_5H_5)]^+$ reacting with $\mathrm{Na[BH_4]}$ to afford the cyclohexadienyl complex $[\mathrm{Ru}(\eta^5\text{-}C_6H_7)(\eta\text{-}C_5H_5)]$ in low yield. Such behaviour is in contrast to the corresponding iron complexes which react with nucleophiles to give high yields of the *exo*-substituted cyclohexadienyl derivatives.[39]

As with the above cases, attempts to react (**9**)—(**12**) with phosphines or phosphites were unsuccessful. However, reaction of (**9**) or (**11**) with $\mathrm{K[BHBu^s_3]}$ in tetrahydrofuran (thf) at −78 °C led in each instance to the formation of a yellow solution, subsequent work-up affording (**14**) and (**15**) (Scheme 9) in almost quantitative yield. These complexes were identified by their mass, ^{1}H and ^{13}C-{^{1}H} n.m.r. spectra and by elemental analysis.

Thus, nucleophilic attack by $[\mathrm{BHBu^s_3}]^-$ on the sandwich cations of (**9**) or (**11**) occurs solely at the cyclopentadienyl ligand. Moreover, reaction of (**9**) with $\mathrm{Li[BDEt_3]}$ led to deuterium incorporation only in the *exo* position (by n.m.r.) indicating that the reaction path is *via* direct attack on the opposite face of the η-C_5H_5 ligand to which the ruthenium is bonded. This difference in chemoselectivity presumably derives from the presence of bulky substituents on the C_6 ring.

Finally, the reduction of (**9**) was examined. Astruc and co-workers[40] and others[41] have shown that one-electron reduction of $[\mathrm{Fe}(\eta^6\text{-arene})(\eta\text{-}C_5H_5)][\mathrm{BF_4}]$ results in reversible formation of the corresponding neutral 19-electron radical species. In contrast, the ruthenium cations $[\mathrm{Ru}(\eta^6\text{-}C_6Me_6)(\eta\text{-}C_5H_5)]^+$ and $[\mathrm{Ru}(\eta^6\text{-}p\text{-}MeC_6H_4CHMe_2)(\eta\text{-}C_5H_5)]^+$ were observed to resist reduction under electrochemical conditions up to the solvent limit.[21]

It was therefore, important to attempt to reduce the bulky cations formed in this study. Under conditions of cyclic voltammetry the complexes $[\mathrm{Ru}(\eta^6\text{-}C_6Ph_6)(\eta\text{-}C_5H_5)][\mathrm{BF_4}]$ (**9**), $[\mathrm{Ru}(\eta^6\text{-}C_6Ph_5Me)(\eta\text{-}C_5H_5)][\mathrm{BF_4}]$ (**10**), and $[\mathrm{Ru}(\eta^6\text{-}C_6Ph_4Me_2)(\eta\text{-}C_5H_5)][\mathrm{BF_4}]$ (**11**) were each found to undergo an irreversible one-electron reduction at −1.59, −1.67, and −1.74 V [*versus* saturated calomel electrode (s.c.e.)], respectively. Furthermore the complete irreversibility of this reduction was observed to be independent of the solvent used (CH_2Cl_2 or thf), and of any variation in the applied scan rate within the range 0.1—1.0 V s^{-1}. These observations suggest that whilst one-electron reduction of the above cations is a comparatively facile process, in each case the initially formed radical (19-electron) species must undergo a further irreversible process which is rapid in comparison with the applied scan rate. It is also interesting to note that the reduction potential shows a corresponding increase with the number of methyl substituents on the arene ligand.

Reduction of (**9**) on a preparative scale was achieved by treating a thf suspension of the material with a sodium amalgam at room temperature. Under these conditions the white suspension rapidly turned to a lemon yellow solution, reaction appearing complete after *ca.* 15 min. Work-up afforded a yellow solid. Examination of the ^{1}H and ^{13}C-{^{1}H} n.m.r. spectra of the product showed it to be a mixture of two compounds, in an approximate 1:1 ratio, one of which was readily identified as the η^4-cyclopentadiene complex (**14**). The other complex present showed, in the ^{1}H n.m.r. spectrum, resonances corresponding to the presence of phenyl protons [δ 7.59—6.67 (m, 30 H)] and cyclopentadienyl protons [δ 4.84 (s, 5 H)], together with a single proton resonance at δ 5.19. The ^{13}C-{^{1}H} spectrum showed resonances at δ 147.5—124.9 (Ph), 83.3 (C_5H_5), 103.0, 99.3, 48.9 (*C*Ph), and 59.1 (*C*HPh), the assignment of these signals being aided by the results of a partially proton-coupled (off-resonance) spectrum. From these data it is evident that this other reaction product is a cyclohexadienyl species [Ru(η^5-C_6Ph_6H)(η-C_5H_5)] (**16**) (Scheme 10), the chemical shifts of the cyclohexadienyl ring carbons agreeing well with published spectra.[42] Since the cyclic voltammogram of (**9**) shows only one irreversible reduction step in the range 0—2.5 V, the most likely reaction pathway to these products would, therefore, appear to be a simple abstraction of H$^{\bullet}$ from the solvent by the initially formed 19-electron radical. Steric constraints imply that hydrogen abstraction would occur on the *exo* face of the arene ring.

Experimental

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

Preparation of [Ru(CO)(η^4-C_4Ph_4)(η-C_5H_5)][BF_4] (**1**).—To a solution of [$Ru_2(CO)_4$(η-C_5H_5)$_2$] (2.50 g, 5.63 mmol) and diphenylacetylene (6.0 g, 33.7 mmol) in CH_2Cl_2 (100 cm^3) silver tetrafluoroborate (2.30 g, 11.28 mmol) was added and the mixture stirred at room temperature overnight. The resulting solution was filtered through Celite to remove precipitated silver and then washed with CH_2Cl_2 (250 cm^3), the filtered washings being added to the main bulk of the solution. The volume of the solvent was reduced *in vacuo* (100 cm^3) and diethyl ether added (100 cm^3) to afford a yellow-orange precipitate of (**1**), which was further washed with Et_2O and dried *in vacuo*. The yield was generally 2.5—3.0 g, 35—42%. In most cases the solid thus obtained was used without purification. However, in some instances the presence of small amounts of an impurity [$Ru(CO)_3$(η-C_5H_5)][BF_4] was detected (i.r.). This was removed by suspending (**1**) in water and adding Na[BH_4] [0.2 mol equivalent based on the molecular weight of (**1**)] resulting in selective reduction of the impurity. Subsequent extraction of the solid with CH_2Cl_2 followed by crystallisation from CH_2Cl_2–Et_2O afforded yellow-orange *crystals* of (**1**) (Found: C, 63.7; H, 3.9. $C_{34}H_{25}BF_4ORu$ requires C, 64.1; H, 4.0%), ν(CO) (CH_2Cl_2) at 2 040s cm^{-1}. N.m.r.: ^{1}H (CD_3NO_2), δ 7.46 (m, 20 H, Ph), 5.60 (s, 5 H, C_5H_5); ^{13}C-{^{1}H} (CD_3NO_2), δ 202.0 (CO), 132.2—129.5 (Ph), 93.7 (C_5H_5), and 93.3 p.p.m. (C_4Ph$_4$).

Preparation of [$Ru(CO)_2$(η^2-PhC_2Ph)(η-C_5H_5)][BF_4] (**3**).—Also isolated on occasions from the preparation of (**1**) was (**3**), obtained by crystallisation of the mother-liquor, in variable yields (0—30%). However, it was found that pure samples of (**3**) could be prepared by an exact replication of the method described by Reger *et al.*[6] for the preparation of the analogous iron complex, in yields of 80% as an orange solid (Found: C, 51.5; H, 3.2. $C_{21}H_{15}BF_4O_2Ru$ requires C, 51.8; H, 3.1%), ν(CO) (CH_2Cl_2) at 2 088s and 2 047s cm^{-1}. N.m.r.: ^{1}H (CD_3NO_2), δ 7.95—7.41 (m, 10 H, Ph), 6.25 (s, 5 H, C_5H_5); ^{13}C-{^{1}H} (CD_3NO_2), δ 194.4 (CO), 134.6—128.1 (Ph), 94.0 (C_5H_5), and 65.2 p.p.m. (PhC_2Ph).

Preparation of [Ru(NCMe)(η^4-C_4Ph_4)(η-C_5H_5)][BF_4] (**2**).—A solution of (**1**) (0.32 g, 0.47 mmol) in acetonitrile (100 cm^3) contained in a water-cooled quartz reactor was irradiated with u.v. light (500-W lamp) for 2.5 h. Volatile material was removed *in vacuo*, and the residue dissolved in CH_2Cl_2 and filtered. Addition of Et_2O gave a red powder, which was collected and recrystallised (0 °C) from CH_2Cl_2–Et_2O to give purple *crystals* of (**2**) (0.20 g, 61%) (Found: C, 64.2; H, 4.0; N, 2.1. $C_{35}H_{28}BF_4NRu$ requires C, 64.6; H, 4.3; N, 2.1%). N.m.r.: ^{1}H (CD_3NO_2), δ 7.44 (m, 20 H, Ph), 5.28 (s, 5 H, C_5H_5), 2.04 (s, 3 H, NCMe); ^{13}C-{^{1}H} (CD_3NO_2), δ 211 (N*C*Me), 132.4—130.1 (Ph), 93.0 (C_5H_5), 89.9 (C_4Ph$_4$), and 4.25 p.p.m. (NC*Me*).

Preparation of [RuBr(η^4-C_4Ph_4)(η-C_5H_5)] (**4**).—(*a*) A solution of (**2**) (0.35 g, 0.54 mmol) and [NMe_4]Br (0.165 g, 1.08 mmol) in CH_2Cl_2 was stirred at room temperature. After 65 h the volume of the solvent was reduced *in vacuo*, and the reaction mixture chromatographed on an alumina packed column. Elution with Et_2O–CH_2Cl_2 (1:5) gave a dark brown band, which was collected and recrystallised from CH_2Cl_2–hexane to give black *crystals* of (**4**) (0.126 g, 33%) (Found: C, 59.4; H, 3.8. $C_{33}H_{25}BrRu{\cdot}CH_2Cl_2$ requires C, 59.4; H, 4.0%). N.m.r.: ^{1}H ($CDCl_3$), δ 7.5—7.1 (m, 20 H, Ph), 4.97 (s, 5 H, C_5H_5); ^{13}C-{^{1}H} ($CDCl_3$), δ 133.2—128.6 (Ph), 91.2 (C_5H$_5$), and 83.5 p.p.m. (C_4Ph$_4$). The mass spectra showed peaks at *m/e* 602 (*P*), 423.1 (*P* – Br), and 356.1 (C_4Ph_4).

(*b*) Ultraviolet irradiation (500-W lamp) of a solution of (**1**) (2.4 g, 3.68 mmol) and [NMe_4]Br (2.3 g, 14.7 mmol) in CH_2Cl_2 contained in a water-cooled quartz reactor gave on column chromatography black crystals of (**4**) (1.0 g, 39%).

Preparation of [RuCl(η^4-C_4Ph_4)(η-C_5H_5)] (**5**).—A solution of (**2**) (0.60 g, 0.92 mmol) and [NMe_4]Cl (0.2 g, 1.83 mmol) in CH_2Cl_2 was stirred at room temperature for 65 h. Column chromatography followed by recrystallisation from CH_2Cl_2–hexane gave brown *microcrystals* of (**5**) (0.31 g, 60%) (Found: Cl, 6.7. $C_{33}H_{25}ClRu$ requires Cl, 6.4%). N.m.r.: ^{1}H ($CDCl_3$), δ 7.5—6.8 (m, 20 H, Ph), 4.94 (s, 5 H, C_5H_5); ^{13}C-{^{1}H} ($CDCl_3$), δ 133.8—128.0 (Ph), 92.1 (C_5H_5), and 84.4 p.p.m. (C_4Ph$_4$). The mass spectrum showed peaks at *m/e* 558 (*P*), 523.0 (*P* – Cl), and 356.1 (C_4Ph_4).

Preparation of [Ru(SC_6H_4Me-4)(η^4-C_4Ph_4)(η-C_5H_5)] (**6**).—A solution of (**2**) (0.55 g, 0.84 mmol) and Na[SC_6H_4Me-4] (0.3 g, 2 mmol) in CH_2Cl_2 was stirred at room temperature for 5 d. The solvent was removed *in vacuo* and the residue chromatographed on an alumina packed column. Elution with hexane afforded a red band which was collected and recrystallised (0 °C) from hexane to give red crystals of (**6**) (0.10 g, 18%) (Found: C, 72.9; H, 5.0; S, 5.2. $C_{40}H_{32}RuS$ requires C, 74.3; H, 5.0; S, 5.0%). N.m.r.: ^{1}H ($CDCl_3$), δ 7.6—7.0 (m, 20 H, Ph), 6.82—6.48 (AA′BB′ system, 4 H, C_6H_4), 4.84 (s, 5 H, C_5H_5), 2.06 (s, 3 H, C_6H_4*Me*); ^{13}C-{^{1}H} ($CDCl_3$), δ 143.1—127.4 (Ph), 91.3 (C_5H_5), 81.2 (C_4Ph$_4$), and 20.6 p.p.m. (Me).

Further elution with Et_2O–hexane (5:2) and crystallisation (–78 °C) from hexane gave yellow *crystals* of (**7**) (0.10 g, 22%) (Found: C, 71.2; H, 4.5. $C_{33}H_{26}ORu$ requires C, 73.5; H, 4.8%). N.m.r.: ^{1}H ($CDCl_3$), δ 7.4—6.7 (m, 20 H, Ph), 4.81 (s, 5 H, C_5H_5), 3.69 (s, 1 H, CH); ^{13}C-{^{1}H} ($CDCl_3$), δ 144.1—124.3 (Ph), 107.15, 101.48 (C^2, C^3), 79.9 (C_5H_5), and 78.4 p.p.m. (C^4).

When the reaction between (**2**) (0.28 g, 0.43 mmol) and Na[SC_6H_4Me-4] (0.14 g, 0.96 mmol) was repeated in CH_2Cl_2 (25 cm^3) containing H_2O (0.1 cm^3) an improved yield (0.10 g, 43%) of (**7**) was obtained.

Protonation of (**7**).—To [Ru{η^5-CH(Ph)C(Ph)C(Ph)C(Ph)O}(η-C_5H_5)] (**7**) (0.10 g, 0.19 mmol) in CH_2Cl_2 (10 cm^3) at − 78 °C was added $HBF_4 \cdot Et_2O$ (27 μl). The solution was allowed to warm to room temperature and stirred for 1.5 h. The volatile material was removed *in vacuo* and the residue washed with Et_2O (2 × 10 cm^3). Recrystallisation from CH_2Cl_2–Et_2O gave off-white *crystals* of (**8**) (0.038 g, 32%) (Found: C, 63.0; H, 4.4. $C_{33}H_{27}BF_4ORu$ requires C, 63.2; H, 4.3%), ν(CO) (CH_2Cl_2) at 1 662s cm^{-1}. N.m.r.: ^1H (CD_2Cl_2), δ 7.98—7.0 (m, 15 H, Ph), 6.20—5.95 [m, 5 H, Ph (co-ordinated)], 5.09 (s, 5 H, C_5H_5), 3.74 (s, 2 H, CH_2); ^{13}C-{^1H} (CD_2Cl_2), δ 197.7 [*C*O(Ph)], 142—128.0 (C^2,C^3, unco-ordinated C_6H_5), 103.4 (*C*CH_2), 87.06, 85.27, 84.92 (co-ordinated C_6H_5), 80.9 (C_5H_5), and 40.2 p.p.m. (CH_2).

Preparation of [Ru(η^6-C_6Ph_6)(η-C_5H_5)][BF_4] (**9**).—(*a*) A solution of (**1**) and diphenylacetylene (0.25 g, 1.4 mmol) in CH_2Cl_2 (50 cm^3) was irradiated with u.v. light (500 W) for 6 h. The volume of the solvent was reduced *in vacuo* and Et_2O added slowly to afford a white *crystalline* precipitate of (**9**) (0.33 g 76%) (Found: C, 71.5; H, 4.5. $C_{47}H_{35}BF_4Ru$ requires C, 71.6; H, 4.4%). N.m.r.: ^1H (CD_3NO_2), δ 7.45—6.92 (m, 30 H, Ph), 6.15 (s, 5 H, C_5H_5); ^{13}C-{^1H}, δ 134.9—128.5 (Ph), 110.0 (*C*$_6$Ph$_6$), and 85.6 p.p.m. (C_5H_5).

(*b*) A solution of (**5**) (0.10 g, 0.18 mmol) and PhC_2Ph (0.13 g, 0.72 mmol) in CH_2Cl_2 (10 cm^3) was treated with Ag[BF_4] (0.035 g, 0.18 mmol), and stirred at room temperature for 2 h. The reaction mixture was filtered through Celite and Et_2O added. The resultant precipitate was collected and recrystallised from CH_2Cl_2–Et_2O to give off-white crystals of (**9**) (0.03 g, 24%).

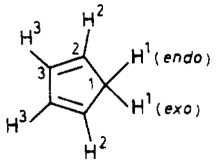
Preparation of [Ru(η^6-C_6Ph_5Me)(η-C_5H_5)][BF_4] (**10**).—Similarly prepared from (**1**) and 1-phenylprop-1-yne was (**10**), obtained as a white microcrystalline solid (65%) (Found: C, 69.3; H, 4.6. $C_{42}H_{33}BF_4Ru$ requires C, 69.5; H, 4.6%). N.m.r.: ^1H (CD_3NO_2), δ 7.68—6.75 (m, 25 H, Ph), 6.05 (s, 5 H, C_5H_5), 2.04 (s, 3 H, Me); ^{13}C-{^1H} (CD_3NO_2), δ 136.0—128.9 (Ph), 111.3 (*C*Ph), 111.0 (*C*Ph), 109.7 (*C*Ph), 101.5 (*C*Me), 85.3 (C_5H_5), and 22.4 p.p.m. (Me).

Preparation of [Ru(η^6-$C_6Ph_4Me_2$-1,2)(η-C_5H_5)][BF_4] (**11**).—Similarly, irradiation of (**1**) and but-2-yne gave white microcrystalline (**11**) (55%) (Found: C, 66.4; H, 4.7. $C_{37}H_{31}BF_4Ru$ requires C, 66.9; H, 4.7%). N.m.r.: ^1H (CD_3NO_2), δ 7.60—6.83 (m, 20 H, Ph), 5.86 (s, 5 H, C_5H_5), 2.33 (s, 6 H, Me); ^{13}C-{^1H} (CD_3NO_2), δ 135.6—128.2 (Ph), 110.9 (*C*Ph), 109.6 (*C*Ph), 101.2 (*C*Me), 84.4 (C_5H_5), and 19.4 p.p.m. (Me).

Preparation of [Ru{η^6-$C_6Ph_4(CO_2Me)_2$-1,2}(η-C_5H_5)][BF_4] (**12**).—In a similar way irradiation of (**1**) and $MeO_2CC_2CO_2Me$ afforded cream crystals of (**12**) (43%) (Found: C, 62.3; H, 4.4. $C_{39}H_{31}BF_4ORu_2$ requires C, 62.3; H, 4.2%), ν(CO) (CH_2Cl_2) at 1 740s cm^{-1}. N.m.r.: ^1H (CD_3NO_2), δ 7.33—7.02 (m, 20 H, Ph), 6.12 (s, 5 H, C_5H_5), 3.66 (s, 6 H, Me); ^{13}C-{^1H} (CD_3NO_2), δ 166.0 (*C*O_2Me), 134.3—128.7 (Ph), 110.9 (*C*Ph), 107.5 (*C*Ph), 96.7 (*C*CO_2Me), 88.0 (C_5H_5), and 55.2 p.p.m. (OMe).

Preparation of [Ru(η^6-C_6Et_6)(η-C_5H_5)][BF_4] (**13**).—Silver tetrafluoroborate (0.46 g, 2.34 mmol) was added to a solution of [$Ru_2(CO)_4(\eta$-$C_5H_5)_2$] (0.52 g, 1.17 mmol) and hex-3-yne (0.95 g, 11.7 mmol) in CH_2Cl_2 (20 cm^3) through which a stream of dry N_2 was passed (CH_2Cl_2 being added when necessary to maintain a constant volume of solvent) for 3 h. After 2 d at room temperature the reaction mixture was filtered through Celite. The volume of the solvent was reduced *in vacuo* to 10 cm^3. Slow addition of Et_2O afforded a beige solid {composed mainly of [Ru(CO)$_3$(η-C_5H_5)][BF_4]}, followed by an oily red-brown material and finally a cream solid. Subsequent recrystallisation of the latter from CH_2Cl_2–Et_2O yielded white *crystals* of (**13**) (0.09 g, 9%) (Found: C, 55.0; H, 7.0. $C_{23}H_{35}BF_4Ru$ requires C, 55.3; H, 7.1%). N.m.r.: ^1H (CD_3NO_2), δ 5.25 (s, 5 H, C_5H_5), 2.69 [q, 12 H, CH_2, *J*(HH) 7.4], 1.34 [t, 18 H, Me, *J*(HH) 7.4 Hz]; ^{13}C-{^1H} (CD_3NO_2), δ 106.9 (*C*$_6$Et$_6$), 81.8 (C_5H_5), 23.1 (CH_2), and 17.4 (Me); ^{13}C-{^1H} (CD_2Cl_2–$CFCl_3$, 143 K), δ 106.4 (*C*Et), 101.9 (*C*Et), 79.7 (C_5H_5), 22.7 (CH_2), 20.7 (CH_2), 19.4 (Me), and 13.7 p.p.m. (Me).

Preparation of [Ru(η^4-C_5H_6)(η^6-C_6Ph_6)] (**14**).—K-[BHBu$^s_3$] (0.24 mmol) was added (−78 °C) to a stirred suspension of (**9**) (0.19 g, 0.24 mmol) in thf (15 cm^3). After 20 min the reaction mixture was allowed to warm to room temperature and the solvent then removed *in vacuo*. The residue was extracted with CH_2Cl_2 (4 cm^3) and chromatographed on alumina. Elution with CH_2Cl_2–Et_2O (1:1) yielded one yellow band, which was collected and recrystallised (−78 °C) from CH_2Cl_2–hexane to give yellow *crystals* of (**14**) (0.15 g, 86%) (Found: C, 80.6; H, 5.2. $C_{47}H_{36}Ru$ requires C, 80.4; H, 5.2%). N.m.r.: ^1H (CD_2Cl_2), δ 7.29—6.71 (m, 30 H, Ph), 5.55 (m, 2 H, H^3), 3.57 [d, 1 H, H^1(*exo*), *J*(HH) 10.1], 3.28 [dt, 1 H, H^1(*endo*), *J*(HH) 10.1, *J* (H^1H^2) 1.7 Hz], 3.15 (m, 2 H, H^2); ^{13}C-{^1H} (CD_2Cl_2), δ 138.7 (*ipso*-Ph), 134.1—126.0 (Ph), 102.5 (*C*$_6$Ph$_6$), 77.1 (C^3), 46.4 (C^1), and 43.4 p.p.m. (C^2). The mass spectrum showed peaks at *m*/*e* 702 (*P*), 625 (*P* − Ph), and 534 (C_6Ph_6).



Preparation of [Ru(η^4-C_5H_6)(η^6-$C_6Ph_4Me_2$-1,2)] (**15**).—Similarly, reaction of (**11**) with K[BHBu$^s_3$] gave the yellow oily solid (**15**) (86%). N.m.r.: ^1H (C_6D_6), δ 7.44—6.59 (m, 20 H, Ph), 5.23 (m, 2 H, H^3), 3.78 [d, 1 H, H^1(*exo*), *J*(HH) 10.0], 3.21 [dt, 1 H, H^1(*endo*), *J*(HH) 10.0, *J*(H^1H^2) 1.7 Hz], 2.88 (m, 2 H, H^2), 1.95 (s, 6 H, Me); ^{13}C-{^1H} (C_6D_6), δ 140.1—125.9 (Ph), 104.4 (*C*Ph), 102.6 (*C*Ph), 91.2 (*C*Me), 75.8 (C^3), 46.4 (C^1), 41.5 (C^2), and 18.6 p.p.m. (Me).

Reaction of [Ru(η^6-C_6Ph_6)(η-C_5H_5)][BF_4] *with* Na–Hg.—A suspension of (**9**) (0.30 g, 0.38 mmol) in thf (25 cm^3) was stirred over sodium amalgam (0.03 g, 1.30 mmol Na in 5 cm^3 of Hg) for 1.5 h at room temperature. The resultant yellow solution was filtered through alumina, reduced in volume *in vacuo* (to *ca.* 5 cm^3) and hexane added, affording a yellow solid. After washing with pentane (2 × 5 cm^3) and drying *in vacuo*, ^1H and ^{13}C n.m.r. spectroscopy showed it to be a mixture of (**14**) and (**16**) (1:1). N.m.r. of (**16**): ^1H (C_6D_6), δ 7.59—6.67 (m, 30 H, Ph), 5.19 (s, 1 H, C*H*Ph), 4.84 (s, 5 H, C_5H_5); ^{13}C-{^1H} (C_6D_6), δ 147.5 (*ipso*-Ph), 145.8 (*ipso*-Ph), 139.6 (*ipso*-Ph), 139.1 (*ipso*-Ph), 136.0—124.9 (Ph), 103.0 (C^1), 99.3 (C^2), 83.3 (C_5H_5), 59.1 (C^4), and 48.9 p.p.m. (C^3).

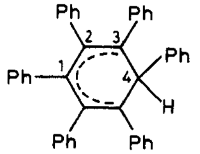


Table 3. Atomic co-ordinates ($\times 10^4$) for complex (**2**)

Atom	*x*	*y*	*z*
Ru	2 245(1)	1 333(1)	3 608(1)
C(1)	4 184(2)	1 060(1)	2 844(2)
C(11)	4 774(3)	1 235(1)	1 712(2)
C(12)	6 186(3)	1 383(1)	1 706(2)
C(13)	6 721(3)	1 572(1)	656(2)
C(14)	5 853(3)	1 616(1)	−388(2)
C(15)	4 462(3)	1 467(1)	−400(2)
C(16)	3 907(3)	1 275(1)	647(2)
C(2)	3 303(2)	657(1)	3 124(2)
C(21)	2 769(3)	241(1)	2 401(2)
C(22)	3 633(3)	60(1)	1 510(2)
C(23)	3 236(3)	−345(1)	841(2)
C(24)	1 967(3)	−573(1)	1 037(3)
C(25)	1 118(3)	−404(1)	1 922(3)
C(26)	1 517(3)	−2(1)	2 611(3)
C(3)	3 537(2)	762(1)	4 442(2)
C(31)	3 224(2)	484(1)	5 537(2)
C(32)	3 135(3)	−16(1)	5 455(2)
C(33)	2 816(3)	−288(1)	6 461(3)
C(34)	2 596(3)	−67(1)	7 556(3)
C(35)	2 704(3)	428(1)	7 655(2)
C(36)	3 013(3)	706(1)	6 656(2)
C(4)	4 434(2)	1 170(1)	4 167(2)
C(41)	5 523(2)	1 451(1)	4 873(2)
C(42)	6 135(3)	1 266(1)	5 969(2)
C(43)	7 219(3)	1 522(1)	6 597(2)
C(44)	7 711(3)	1 952(1)	6 147(2)
C(45)	7 135(3)	2 130(1)	5 049(3)
C(46)	6 049(3)	1 879(1)	4 420(2)
C(51)	363(3)	986(1)	4 291(3)
C(52)	565(3)	1 422(1)	4 972(3)
C(53)	450(3)	1 799(1)	4 139(3)
C(54)	115(3)	1 602(1)	2 945(3)
C(55)	27(3)	1 104(1)	3 050(3)
C(6)	3 238(3)	2 290(1)	2 294(2)
C(7)	3 610(4)	2 703(1)	1 555(3)
N	2 973(2)	1 962(1)	2 853(2)
F(1)	753(2)	−1 970(1)	1 130(2)
F(2)[a]	−442(4)	−1 392(2)	141(4)
F(3)[a]	−1 522(4)	−2 093(2)	337(5)
F(4)[a]	−1 130(3)	−1 614(2)	1 945(3)
F(5)[b]	−761(17)	−1 340(5)	862(16)
F(6)[b]	−1 092(14)	−2 000(5)	1 999(11)
F(7)[b]	−1 039(17)	−2 070(9)	−56(14)
B	−586(3)	−1 789(1)	928(3)

[a] Site occupancy 0.8181. [b] Site occupancy 0.1819.

Table 4. Atomic co-ordinates ($\times 10^4$) for complex (**7**)

Atom	*x*	*y*	*z*
Ru	1 899(1)	2 067(1)	2 068(1)
C(1)	1 618(2)	3 200(4)	3 073(3)
C(2)	1 240(2)	3 025(4)	2 356(3)
C(3)	1 079(2)	2 001(4)	2 098(4)
C(4)	1 255(2)	1 159(4)	2 623(3)
C(11)	1 407(1)	4 953(3)	3 627(3)
C(12)	1 554	5 874	4 018
C(13)	2 066	6 077	4 168
C(14)	2 431	5 359	3 927
C(15)	2 283	4 438	2 536
C(16)	1 772	4 235	3 386
C(21)	515(1)	4 109(3)	1 845(3)
C(22)	319	4 941	1 369
C(23)	642	5 582	877
C(24)	1 161	5 390	861
C(25)	1 358	4 557	1 337
C(26)	1 035	3 917	1 829
C(31)	861(1)	2 221(3)	391(3)
C(32)	529	2 077	−350
C(33)	72	1 570	−212
C(34)	−54	1 208	668
C(35)	278	1 353	1 409
C(36)	735	1 859	1 271
C(41)	1 079(2)	−522(3)	3 239(2)
C(42)	1 002	−1 564	3 159
C(43)	1 014	−2 024	2 288
C(44)	1 102	−1 442	1 497
C(45)	1 178	−400	1 576
C(46)	1 167	60	2 447
C(50)	2 218(2)	2 385(5)	717(4)
C(51)	2 118(2)	1 333(6)	798(4)
C(52)	2 426(2)	947(5)	1 498(5)
C(53)	2 711(2)	1 754(6)	1 858(4)
C(54)	2 585(2)	2 643(5)	1 375(4)
O(1)	1 839(1)	2 454(3)	3 496(2)

Structure Analyses of [Ru(NCMe)(η^4-C_4Ph_4)(η-C_5H_5)][BF_4] (**2**) *and* [Ru{η^5-CH(Ph)C(Ph)C(Ph)C(Ph)O}(η-C_5H_5)] (**7**).—*Crystal data for* (**2**). $C_{35}H_{28}BF_4NRu$, M = 650.5, monoclinic, space group $P2_1/c$ (no. 14), a = 9.450(2), b = 27.824(6), c = 11.014(2) Å, β = 92.96(2)°, U = 2 892(1) Å^3, Z = 4, D_c = 1.49 g cm^{-3}, F(000) = 1 320, T = 230 K, μ(Mo-K_α) = 5.80 cm^{-1}. Crystal faces [distances from origin (mm)]: (100) [0.24], $(\bar{1}00)$ [0.24], (010) [0.11], $(0\bar{1}0)$ [0.11], (001) [0.2], $(00\bar{1})$ [0.2].

Crystal data for (**7**). $C_{33}H_{26}ORu$, M = 539, orthorhombic, space group *Pbca* (no. 61), a = 26.411(5), b = 13.197(3), c = 14.418(2) Å, U = 5 026(2) Å^3, Z = 8, D_c = 1.43 g cm^{-3}, F(000) = 2 207, T = 298 K, μ(Mo-K_α) = 6.33 cm^{-1}. Crystal faces [distances from origin (mm)]: (001) [0.125], $(00\bar{1})$ [0.125], (100) [0.25], $(\bar{1}00)$ [0.25], $(3\bar{2}0)$ [0.275], $(\bar{2}0\bar{1})$ [0.275], (130) [0.275], $(\bar{1}0\bar{2})$ [0.175].

Diffraction measurements were made using Nicolet *P*3*m* diffractometers on both (**2**) and (**7**) using graphite-monochromated Mo-K_α *X*-radiation (λ = 0.710 69 Å). The crystals of approximate dimensions 0.5 × 0.2 × 0.4 mm for (**2**) and 0.5 × 0.55 × 0.25 for (**7**) were mounted in thin-walled glass capillaries under N_2 in both cases. Intensity data were collected, at reduced temperature (230 K) for (**2**) and at ambient temperature for (**7**), by θ–2θ scans for unique volumes of reciprocal space in the range $4 < 2\theta < 50°$. Absorption corrections were applied to each data set by Gaussian quadrature based on the indexed crystal faces and dimensions, giving transmission coefficients between 0.879 and 0.752 for (**2**) and 0.853 and 0.778 for (**7**). Structure solution and refinement was by Patterson, Fourier, and blocked-cascade full-matrix least-squares methods. Of 5 825 intensity data recorded for (**2**), 4 893 unique observations remained after deletion of systematic absences, and averaging of duplicate and symmetry equivalent intensities, of these 4 257 with $I > 1.5\sigma(I)$ were retained for structure solution and refinement. The corresponding values were 3 720, 3 265, and 2 506 respectively for (**7**).

For (**2**) all non-hydrogen atoms, including both components of the disordered BF_4 ion were refined freely with anisotropic displacement parameters. The BF_4 group showed a two-site disorder in which one fluorine and the boron retained full occupancy and the remaining fluorines occupied two sets of positions at occupancies 0.818 and 0.182. The hydrogen atoms were refined freely with common isotropic displacement parameters for the methyl, cyclopentadienyl, and phenyl group atoms. Final residual indices were R 0.0306, R' 0.0327 and

S 1.208* with weights $w = [\sigma_c^2(F_o) + gF_o^2]^{-1}$ where g (= 0.0006) was chosen to minimise the radiation of S as a function of F_o. For (**7**) the phenyl rings were constrained to local D_{6h} symmetry with C–C = 1.395 Å. All non-hydrogen atoms were assigned anisotropic displacement parameters. All hydrogens were constrained to idealised geometries (C–H = 0.96 Å) with fixed isotropic displacement parameters = 1.2 times those of their attached carbon atom, but with the exception of H(4) which was refined isotropically without constraints. Final residual indices for (**7**) were R 0.0434, R' 0.0411, and S = 1.011 where weights were assigned as for (**2**) with g = 0.005. Final difference electron-density syntheses for (**2**) and (**7**) showed no features outside the ranges + 0.4 to −0.5 e Å^{-3} and +0.5 to −0.5 e Å^{-3} respectively. Tables 3 and 4 list the final atomic co-ordinates for (**2**) and (**7**) respectively.

All calculations were carried out with the SHELXTL programs of the Nicolet *R3m/E* structure determination system, using complex neutral-atom scattering factors taken from ref. 43.

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* $R = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$, $R' = \Sigma w^{\frac{1}{2}}(|F_o| - |F_c|)/\Sigma w^{\frac{1}{2}}|F_o|$, $S = \Sigma w(|F_o| - |F_c|)^2/(\text{n.o.} - \text{n.v.})$; n.o. = number of data, n.v. = number of least-squares variables [n.v. = 493 for (**2**) and 272 for (**7**)].

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