Reaction of Cationic Cyclobutadieneruthenium Complexes with Hydride Anion Donors; Evidence for the Formation of η^4 (5e) Butadienyl Species and Fragmentation of the Cyclobutadiene Ring: Crystal Structures of $[Ru{=}C(Ph){-}\eta^3\text{-}\{C(Ph){\cdot}CH(Ph){\cdot}CH(Ph)\}(\eta\text{-}C_5H_5)]$ and $[Ru_2(\mu\text{-}CO)\{\mu\text{-}(Z)\text{-}C(Ph){=}CH(Ph)\}(CO)_2(\eta^4\text{-}C_4Ph_4)(\eta\text{-}C_5H_5)]$

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Reaction of $[Ru(NCMe)(\eta^4\text{-}C_4Ph_4)(\eta\text{-}C_5H_5)][BF_4]$ with $K[BHBu^s_3]$ affords the η^4 (5e) butadienyl complex $[Ru{=}C(Ph){-}\eta^3\text{-}\{C(Ph){\cdot}C(Ph){\cdot}CH(Ph)\}(\eta\text{-}C_5H_5)]$, whereas a similar reaction with $[Ru(CO)(\eta^4\text{-}C_4Ph_4)(\eta\text{-}C_5H_5)][BF_4]$ affords $[Ru{=}C(Ph){-}\eta^3\text{-}\{C(Ph){\cdot}C(Ph){\cdot}C(Ph)CHO\}(\eta\text{-}C_5H_5)]$ and the μ-vinyl complex $[Ru_2(\mu\text{-}CO)\{\mu\text{-}(Z)\text{-}C(Ph){=}CH(Ph)\}(CO)_2(\eta^4\text{-}C_4Ph_4)(\eta\text{-}C_5H_5)]$.

Transition metal carbene and carbyne complexes continue to attract attention because of their potential reactivity. In exploring the behaviour of the cationic η^4-cyclobutadiene complexes $[Ru(CO)(\eta^4\text{-}C_4Ph_4)(\eta\text{-}C_5H_5)][BF_4]$ (**1**) and $[Ru(NCMe)(\eta^4\text{-}C_4Ph_4)(\eta\text{-}C_5H_5)][BF_4]$ (**2**) (ref. 1) towards hydride anion donors we have observed unusual ring-opening reactions and the formation of novel η^4 (5e) butadienyl complexes containing a metal to carbon multiple bond.

Addition [−78 °C, tetrahydrofuran (thf)] of $K[BHBu^s_3]$ to (**2**) leads to a rapid reaction and the formation (85% yield) of an air-sensitive purple crystalline complex (**3**) (Scheme 1). Elemental, mass, and n.m.r. spectral analysis[†] suggested the molecular formula $[Ru\{C(Ph){\cdot}C(Ph){\cdot}C(Ph){\cdot}CHPh\}(\eta\text{-}C_5H_5)]$ for (**3**), and significantly the $^{13}C\{^1H\}$ n.m.r. spectrum showed a low field signal at δ 245.96 characteristic of a terminal alkylidene type carbon implying the presence of a ruthenium to carbon multiple bond. This was confirmed by single crystal *X*-ray crystallography.[‡] The molecular geometry

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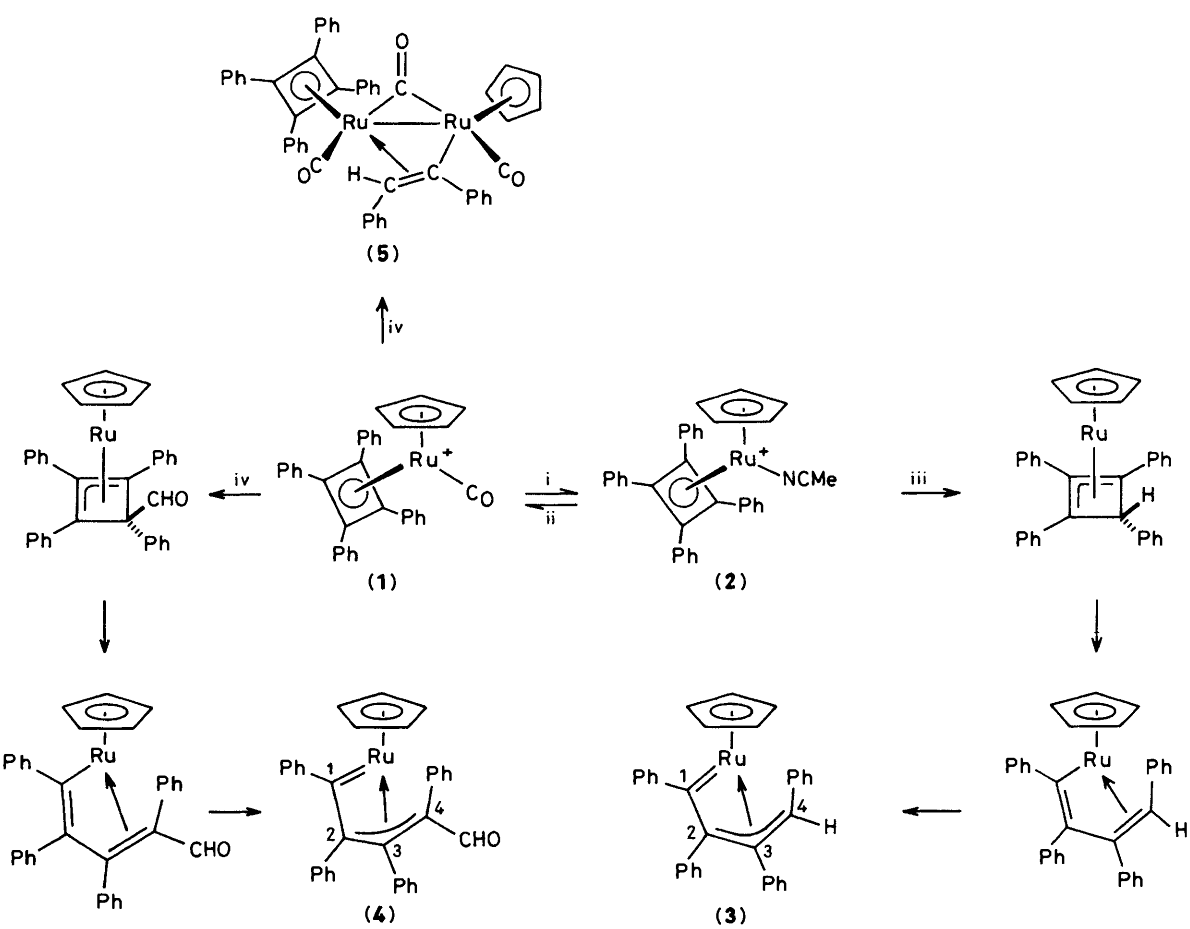
[†] Selected spectroscopic data for compound (**3**): N.m.r. ^1H (C_6D_6), δ 7.56—6.42 (m, 20 H, Ph), 4.89 (s, 5 H, C_5H_5), 4.24 (s, 1 H, CHPh); $^{13}C\{^1H\}$ $(C_6D_5CD_3)$, δ 245.96 [C(1)], 151.45—123.32 (Ph), 97.53 [C(3)], 94.95 [C(2)], 82.59 (C_5H_5), 55.09 [C(4)]; ^1H coupled ^{13}C (C_6D_6), δ 248.78 [t, C(1), $^3J(CH)$ 4.6 Hz], 100.07 [t, C(3), $^3J(CH)$ 4.1 Hz], 97.91 [t, C(2), $^3J(CH)$ 4.1 Hz], 85.11 [d of quintets, C_5H_5, $^1J(CH)$ 175.7, $^2J(CH)$ 6.6 Hz], 57.58 [d, C(4), $^1J(CH)$ 147.6 Hz]. Compound (**4**): ν_{CO} 1 643 cm^{-1} (CH_2Cl_2); n.m.r. ^1H (CD_3NO_2), δ 9.28 (s, 1 H, CHO), 7.41—6.56 (m, 20 H, Ph), 5.44 (s, 5 H, C_5H_5); $^{13}C\{^1H\}$ (CD_3NO_2), 255.23 [C(1)], 192.01 (CHO), 147.61—125.05 (Ph), 109.52 [C(3)], 98.02 [C(2)], 86.00 (C_5H_5), 73.77 [C(4)]; ^{13}C nuclear Overhauser enhancement (CD_3NO_2), δ 253.01 [s, C(1)], 192.46 [d, CHO, $J(CH)$ 176.4 Hz], 109.94 [t, C(3), $^3J(CH)$ 3.3 Hz], 98.36 [t, C(2), $^3J(CH)$ 3.3 Hz], 86.46 [d of quintets, C_5H_5, $^1J(CH)$ 176.6, $^2J(CH)$ 6.6 Hz], 73.64 [t, C(4), $^3J(CH)$ 2.8 Hz]. Compound (**5**), ν_{CO} 1 969m, 1 933s, 1 795m cm^{-1} (CH_2Cl_2); n.m.r. ^1H $[(CD_3)_2CO]$, δ 7.34—6.63 (m, 30 H, Ph), 4.94 (s, C_5H_5), 2.83 (s, 1 H, C*H*Ph).

[‡] *Crystal data* for (**3**): $C_{33}H_{26}Ru$, $M = 523.6$, triclinic, space group $P\bar{1}$, $a = 10.156(4)$, $b = 10.996(4)$, $c = 13.145(6)$ Å, $\alpha = 112.12(3)$, $\beta = 101.20(3)$, $\gamma = 103.76(3)°$, $U = 1253.4(9)$ Å^3, $Z = 2$, $D_c = 1.39$ g cm^{-3}, $F(000) = 535.94$ electrons, $\mu(Mo\text{-}K_\alpha) = 6.30$ cm^{-1}, $\lambda = 0.71069$ Å. The structure was solved by heavy atom (Patterson and Fourier) methods and refined using blocked cascade least squares with all non hydrogen atoms anisotropic. All hydrogen atoms were located in the difference map, but all except H(4), which was allowed to refine freely, were fixed in idealised positions and refined isotropically. For 3 319 unique, observed $[I > 2\sigma(I)]$ reflections collected at 293 K on a Nicolet P3m diffractometer the current R factor is 0.044 (R_w 0.0421).

Crystal data for (**5**) as its diethyl ether solvate: $C_{50}H_{36}O_3\text{-}Ru_2{\cdot}C_4H_{10}O$, $M = 961.1$, monoclinic, $P2_1/c$ (No. 14), $a = 15.763(11)$, $b = 15.928(9)$, $c = 18.914(9)$ Å, $\beta = 112.58(5)°$, $U = 4\,385(5)$ Å^3, $Z = 4$, $D_c = 1.46$ g cm^{-3}, $F(000) = 1\,960$ electrons, $\mu(Mo\text{-}K_\alpha) = 19.0$ cm^{-1}, $\bar{\lambda} = 0.710\,69$ Å. For 3 014 unique, observed $[I > 2\sigma(I)]$ intensity data collected at 293 K on a Nicolet P3m diffractometer the current R factor is 0.054 (R_w 0.051). Structure solution and refinement as for (**3**) with H(9) being the only hydrogen atom freely refined.

The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.



Scheme 1. i, u.v., MeCN; ii, CO; iii, K[$BHBu^s_3$], thf, −MeCN; iv, K[$BHBu^s_3$], thf.

is shown in Figure 1 and establishes that a ring-opening reaction has occurred, the hydride being located on a terminal carbon C(4) of a butadienyl system. All four carbon atoms of the C_4 chain are bonded to the Ru(η-C_5H_5) fragment, although one of the carbons C(1) is an alkylidene (carbene) carbon doubly bonded to Ru as evidenced by a Ru–C(1) distance of 1.896(5) Å (ref. 2). The remaining three carbon atoms have Ru–C(2), Ru–C(3), and Ru–C(4) distances of 2.204(5), 2.152(4), and 2.154(6) Å, respectively, which are characteristic[3] of an η^3-allylic system. Twisting of the C_4 chain, reflected in the torsion angles (see Figure 1), allows η^4-bonding to the ruthenium centre.

Thus, the butadienyl system present in (**3**) adopts a novel bonding mode. It is suggested that the C_4 open chain system is formed by a conrotatory ring-opening reaction of an η^3-cyclobutenyl complex (Scheme 1). Loss of the co-ordinated acetonitrile generates a co-ordinatively unsaturated ruthenium centre. In trying to accommodate this unsaturation the η^3 (3e) butadienyl system [for a similar system in 18e Ru(η-C_5H_5) chemistry see ref. 4] twists and bonds as an η^4 (5e) system, and in doing so generates a ruthenium to carbon double bond, a potential site for further reactions. Such behaviour has not been observed previously, although a possible parallel can be seen with η^2/η^1-vinyl species.[5,6]

The *X*-ray crystal structure determination shows that the hydrogen atom delivered by the [$BHBu^s_3$]$^-$ anion occupies a pseudo-*syn* environment, and therefore, the unsaturation at

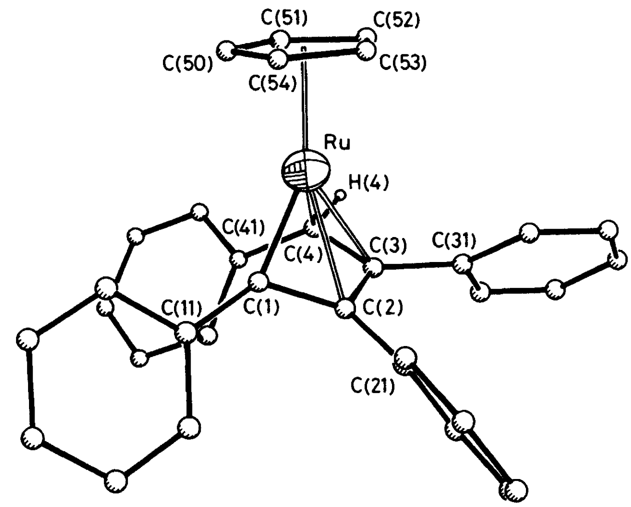


Figure 1. Molecular structure of (**3**) showing atomic labelling scheme. Important geometric parameters include: lengths, Ru–C(1) 1.896(5), Ru–C(2) 2.204(5), Ru–C(3) 2.152(4), Ru–C(4) 2.154(6), C(1)–C(2) 1.419(5), C(2)–C(3) 1.435(7), C(3)–C(4) 1.445(7) Å. Angles: Ru–C(1)–C(2) 32.0(3), C(2)–C(3)–C(4) 119.4(3)°. Torsion angles: Ru–C(1)–C(2)–C(3) −43.4(4), C(11)–C(1)–C(2)–C(21) −39.8(8), C(1)–C(2)–C(3)–C(4) −15.9(7), C(2)–C(3)–C(4)–C(41) −53.4(7), C(2)–C(3)–C(4)–H(4) 162(3)°.

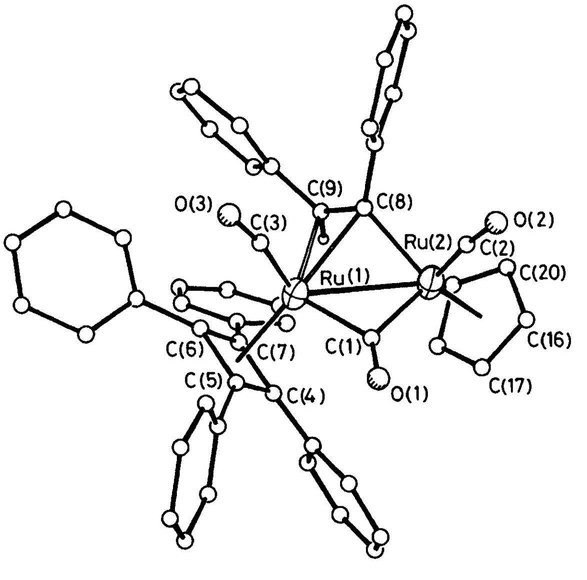


Figure 2. Molecular structure of (**5**) showing atomic labelling scheme, phenyl and cyclopentadienyl hydrogens omitted for clarity. Important geometric parameters include: Ru(1)–Ru(2) 2.802(2), Ru(1)–C(8) 2.313(10), Ru(2)–C(8) 2.073(11), Ru(1)–C(9) 2.368(9), C(8)–C(9) 1.413(15), Ru(1)–C(4) 2.375(9), Ru(1)–C(5) 2.157(9), Ru(1)–C(6) 2.165(11), Ru(1)–C(7) 2.347(10), Ru(1)–C(3) 1.887(13), Ru(1)–C(1) 2.058(12), Ru(2)–C(1) 2.066(12), Ru(2)–C(2) 1.853(13), Ru(2)–C(cyclopentadienyl) av. 2.267(12) Å.

the ruthenium centre could not be satisfied by an agostic RuHC interaction. It is interesting to note that in the palladium–butadienyl[7] system [Pd{C(CO_2Me)·C(CO_2Me)·C(CO_2Me)·C(CO_2Me)–μ-H}$(PPh_3)_2$Br] the $CHCO_2Me$ group has the correct orientation to allow a PdHC interaction. If, as mentioned above, (**3**) is formed in a conrotatory ring-opening reaction then the observed stereochemistry of (**3**) requires that the hydride anion be delivered, presumably *via* the metal, to the *endo*-face of the cyclobutadiene ring rather than the expected *exo*-face.

In contrast, the reaction (−50 °C, thf) between the carbonyl cation (**1**) and K[$BHBu^s_3$] afforded two products, which were obtained as dark green (**4**) (12%) and orange (**5**) (20%) crystalline materials. Elemental analysis and n.m.r. and i.r. spectroscopy† suggested the illustrated structure for (**4**), the $^{13}C\{^1H\}$ n.m.r. spectrum showing a characteristic low field signal at δ 255.23, and the presence of a CHO group being indicated by a strong band in the i.r. spectrum at 1 643 cm^{-1}. The last structural feature was confirmed by a proton-coupled ^{13}C n.m.r. spectrum, which showed a resonance at δ 192.01 [d, CHO, *J*(CH) 176.4 Hz], the corresponding spectrum of the deuterio-analogue obtained from a reaction with K[$BDEt_3$], exhibiting a triplet at δ 189.22 [CDO, *J*(CD) 25.6 Hz]. Thus, (**4**) is also an η^4 (5e) butadienyl complex, structurally related to (**3**), where the C*H*Ph substituent is replaced by a CHO group in the analogous pseudo *syn* position. An obvious reaction pathway to (**4**) involves nucleophilic attack on co-ordinated CO, migration of the resultant formyl group onto the *endo*-face of the cyclobutadiene followed by a conrotatory ring-opening reaction of the resultant cyclobutenyl complex.

A single crystal *X*-ray study‡ was required in order to establish the structure of (**5**). As shown in Figure 2, molecules of (**5**) in the solid state consist of two ruthenium atoms, Ru(1) and Ru(2), at a single-bond distance of 2.802(2) Å, bridged by carbonyl and (*Z*)-1,2-diphenylvinyl ligands, each ruthenium carrying a terminal carbonyl ligand, and further co-ordinated by η^4-tetraphenylcyclobutadiene and η-cyclopentadienyl ligands, respectively. The $Ru_2(CO)_2(\mu\text{-}CO)$ unit shows *cis*-stereochemistry. The μ-vinyl ligand has phenyl rings as *cis* substituents, and the CHPh group *syn* to the cyclopentadienyl group in contrast to the preference for *anti* orientation shown by [C(Ph)·CHPh] in the cation $[Ru_2(CO)_2(\mu\text{-}CO)\{\mu\text{-}C(Ph)\text{=}CPh\}(\eta\text{-}C_5H_5)_2]^+$ (ref. 8). The η-C_4Ph_4 ring is somewhat asymmetrically bound to Ru(1), *i.e.* tending towards η^2. Those ring carbon atoms [C(4), C(7), see Figure 2], which are furthest from Ru(1), are most nearly *trans* to C(3) [C(3)–Ru(1)–C(ring) angles are 137.3(4), 99.3(4), 91.6(5), and 127.6(5)° for C(4)—(7), respectively], and are involved in short contacts with the vinyl and η-cyclopentadienyl ligands. This reaction involves a carbon–carbon bond fragmentation of the η^4-cyclobutadiene ring, for which there is no precedent. It is possible that an intermediate η^1-butadienyl complex undergoes either a β-alkyl elimination reaction or a ruthenium–hydrogen promoted 1,6-fragmentation reaction. These reaction pathways will be discussed in a full paper.

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