

The Synthesis, Structure, and Reactivity of Cationic η^4 -Cyclobutadiene–Ruthenium Complexes; Formation of the Trisethylene(η -cyclopentadienyl)ruthenium Cation

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Reaction of $[\text{Ru}(\text{CO})_2(\eta\text{-C}_5\text{H}_5)]_2$ with AgBF_4 and PhC_2Ph affords $[\text{Ru}(\text{CO})(\eta^4\text{-C}_4\text{Ph}_4)(\eta\text{-C}_5\text{H}_5)][\text{BF}_4]$, which on u.v. irradiation in MeCN gives $[\text{Ru}(\text{NCMe})(\eta^4\text{-C}_4\text{Ph}_4)(\eta\text{-C}_5\text{H}_5)][\text{BF}_4]$ identified by X-ray crystallography; similar irradiation of the carbonyl cation in the presence of alkynes or ethylene gives the sterically hindered arene cations $[\text{Ru}(\eta^6\text{-arene})(\eta\text{-C}_5\text{H}_5)][\text{BF}_4]$ and $[\text{Ru}(\eta^2\text{-C}_2\text{H}_4)_3(\eta\text{-C}_5\text{H}_5)][\text{BF}_4]$.

Although cyclobutadiene metal complexes^{1,2} have played an important role in the development of organometallic chemistry, relatively little is known about cationic species, and their synthetic potential has not been exploited. In attempting to synthesise cationic alkyne complexes where the alkyne functions as a four-electron donor,³ we have obtained the first

examples of η^4 -cyclobutadiene–ruthenium cations. These are reactive molecules and they undergo interesting ring expansion reactions with alkynes and alkenes providing synthetic pathways to η^6 -arene(η -cyclopentadienyl)ruthenium and trisethylene(η -cyclopentadienyl)ruthenium cations.

Addition of AgBF_4 to a solution of $[\text{Ru}(\text{CO})_2(\eta\text{-C}_5\text{H}_5)]_2$

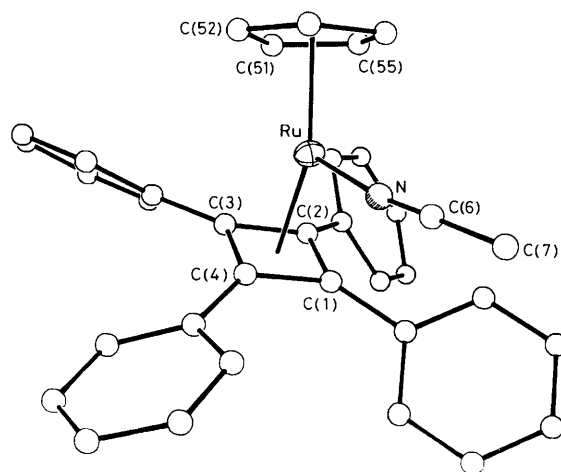
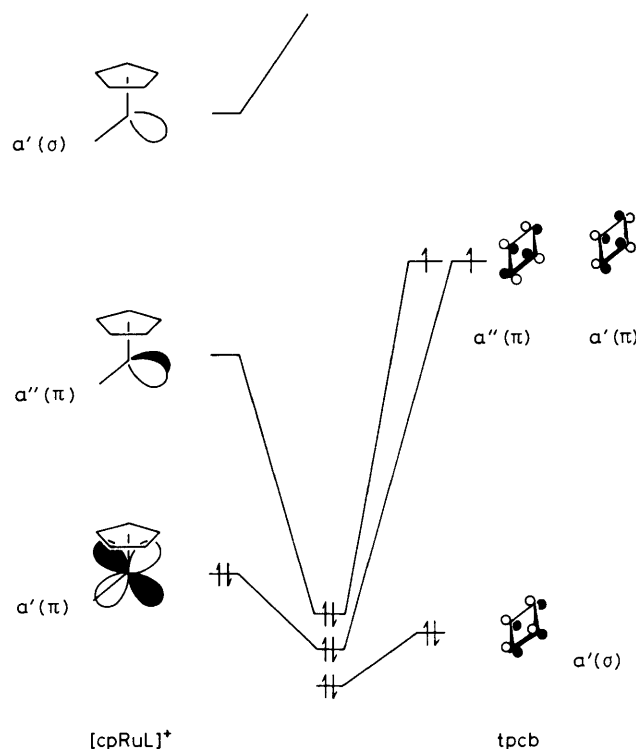


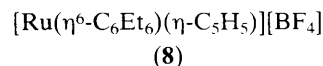
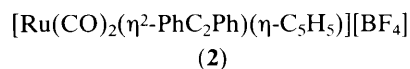
Figure 1. Molecular structure of $[\text{Ru}(\text{MeCN})(\eta\text{-C}_4\text{Ph}_4)(\eta\text{-C}_5\text{H}_5)]^+$ (**3**) showing the atomic labelling scheme. Important geometric parameters include: lengths Ru–C(51) 2.191(3), Ru–C(52) 2.255(3), Ru–C(53) 2.237(3), Ru–C(54) 2.234(3), Ru–C(55) 2.246(3), Ru–N 2.070(2), N–C(6) 1.135(4), C(51)–C(52) 1.433(4), C(52)–C(53) 1.396(4), C(53)–C(54) 1.446(5), C(54)–C(55) 1.391(5), C(51)–C(55) 1.426(4) Å; angles C(4)–C(1)–C(2) 90.8(2), C(1)–C(2)–C(3) 89.9(2), C(2)–C(3)–C(4) 90.5(2), C(1)–C(4)–C(3) 88.8(2)°.

and diphenylacetylene in CH_2Cl_2 leads to a redox reaction, and the formation of a separable mixture of $[\text{Ru}(\text{CO})(\eta^+\text{-C}_4\text{Ph}_4)(\eta\text{-C}_5\text{H}_5)][\text{BF}_4]$ (**1**)[†] (47% yield), $[\text{Ru}(\text{CO})_2(\eta^2\text{-PhC}_2\text{Ph})(\eta\text{-C}_5\text{H}_5)][\text{BF}_4]$ (**2**), and $[\text{Ru}(\text{CO})_3(\eta\text{-C}_5\text{H}_5)][\text{BF}_4]$. The remaining terminal carbonyl ligand in (**1**) is photolabile and u.v. irradiation in acetonitrile affords $[\text{Ru}(\text{NMe})(\eta^+\text{-C}_4\text{Ph}_4)(\eta\text{-C}_5\text{H}_5)][\text{BF}_4]$ (**3**) in high yield (92%). Reaction of (**3**) with CO (10 atm) regenerates (**1**). The structural identity of (**3**) was established by single crystal X-ray diffraction studies,[‡] the results of which are illustrated in Figure 1. The cation contains a ruthenium atom co-ordinated by η-cyclopentadienyl (cp), η-tetraphenylcyclobutadiene (tpcb), and acetonitrile ligands. The co-ordination of the tpcb to ruthenium is only



Scheme 1. Qualitative interaction diagram for $d^6\text{-}[\text{cpRuL}]^+$ and C_4R_4 fragments.

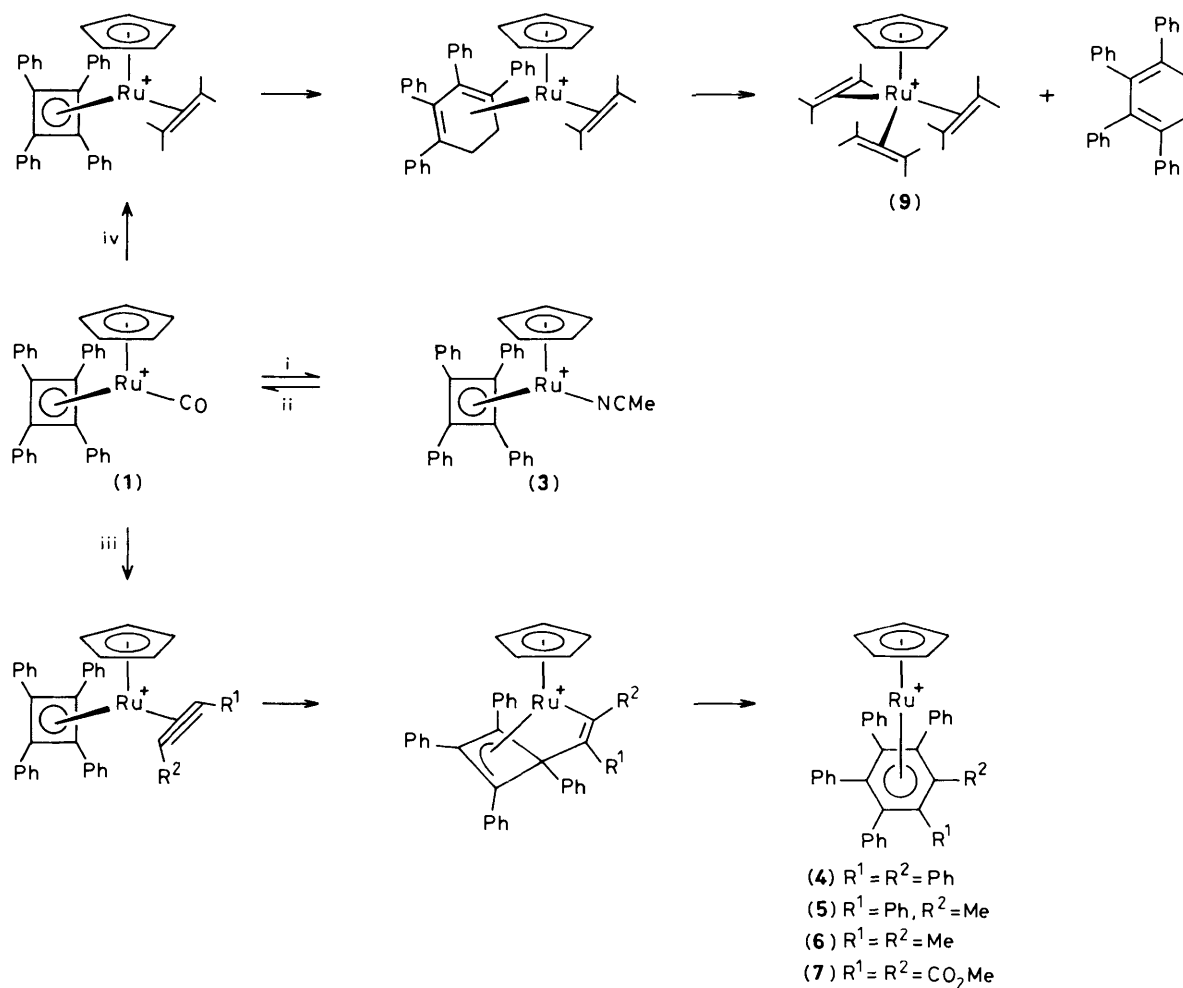
approximately symmetrical; Ru–C distances are 2.192(2), 2.208(3), 2.177(2), and 2.175(2) Å for C(1), C(2), C(3), and C(4), respectively. The C(1)–C(2) and C(3)–C(4) bonds lie nearly parallel to the Ru, N, tpcb, cp plane, deviating by 10.2 and 10.7°, respectively. The tpcb ring is markedly rectangular with C(1)–C(2) and C(3)–C(4) short and C(2)–C(3) and C(1)–C(4) long [1.438(2), 1.457(2), 1.486(3), and 1.497(3) Å respectively, *cf.* C(ring)–C(Ph) 1.478 ± 0.003 Å]. This distortion can be traced to the nature of the frontier orbitals⁴ of the $d^6\text{-cpRuL}^+$ fragment (see Scheme 1) which break the degeneracy of the e_g set of cyclobutadiene orbitals [$e_g \rightarrow a' + a''$ in the approximate C_4 point group of (**3**)], and bring about greater occupancy of the a'' (relative to a') cyclobutadiene m.o. leading to the observed bond length variation. The C–C bond lengths within the η-cyclopentadienyl ring show a complementary variation due to the effect of the tpcbRuL²⁺ fragment on the e_1'' orbitals.



Recent studies⁵ on the reversibility of η¹-cyclobutadiene-cobalt formation from complexed alkynes suggest that the immediate precursor of (**1**) is the bisalkyne cation $[\text{Ru}(\text{CO})(\eta^2\text{-PhC}_2\text{Ph})_2(\eta\text{-C}_5\text{H}_5)]^+$ rather than a Ru^{IV} metalla cyclopentadiene. However, an attempt to generate this intermediate by irradiating (u.v.) the monoalkyne cation (**2**) in the presence of PhC_2Ph led instead to the formation of the sterically crowded hexaphenylbenzene complex $[\text{Ru}(\eta^6\text{-C}_6\text{Ph}_6)(\eta\text{-C}_5\text{H}_5)][\text{BF}_4]$ (**4**). Suspecting that (**4**) might be

[†] Selected spectroscopic data for (**1**): ν_{CO} 2 040 cm^{-1} (CH_2Cl_2); n.m.r. (CD_3NO_2) ^1H , δ 7.46 (m, 20 H, Ph), 5.60 (s, 5 H, C_5H_5); ^{13}C - $\{^1\text{H}\}$, δ 201.99 (CO), 132.18–129.45 (Ph), 93.71 (C_5H_5), 93.26 (C_4Ph_4). (**2**): ν_{CO} 2 088 and 2 047 cm^{-1} (CH_2Cl_2); n.m.r. (CD_3NO_2) ^{13}C - $\{^1\text{H}\}$, δ 194.44 (CO), 134.58–128.09 (Ph), 94.03 (C_5H_5), 62.25 (PhC_2Ph). (**3**): n.m.r. (CD_3NO_2) ^1H , δ 7.44 (m, 20 H, Ph), 5.28 (s, 5 H, C_5H_5), 2.04 (s, 3 H, NMe). (**4**): n.m.r. (CD_3NO_2) ^1H , δ 7.45–6.92 (m, 30 H, Ph), 6.15 (s, 5 H, C_5H_5); ^{13}C - $\{^1\text{H}\}$, δ 134.93–128.49 (Ph), 109.97 (C_6Ph_6), 85.59 (C_5H_5). (**8**): n.m.r. (CD_3NO_2) ^1H , δ 5.25 (s, 5 H, C_5H_5), 2.69 [q, 12 H, CH_2CH_3 , $J(\text{HH})$ 7.5 Hz], 1.34 [t, 18 H, CH_2CH_3 , $J(\text{HH})$ 7.5 Hz]; ^{13}C - $\{^1\text{H}\}$, δ 106.91 (C_6Et_6), 81.79 (C_5H_5), 23.06 (CH_2), 17.44 (CH_3).

[‡] Crystal data for (**3**)· BF_4 : $\text{C}_{35}\text{H}_{28}\text{NRuBF}_4$, $M = 650.5$; monoclinic, space group $P2_1/c$ (No. 14), $a = 9.450(2)$, $b = 27.824(6)$, $c = 11.014(2)$ Å, $\beta = 92.96(2)^\circ$, $U = 2892(1)$ Å³, $Z = 4$, $D_c = 1.49$ g cm^{-3} , $F(000) = 1320$, $\mu(\text{Mo-K}\alpha) = 5.80$ cm^{-1} . The structure was solved by heavy atom (Patterson and Fourier) methods and refined by a least squares procedure. For 4253 unique, observed [$I > 1.5\sigma(I)$], absorption corrected, intensity data collected at 230 K on a Nicolet P3m diffractometer the current residual R is 0.031. The atomic coordinates for this structure 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 2. i, U.v. in MeCN; ii, + CO; iii, u.v. + $R^1C_2R^2$; iv, u.v. + C_2H_4 . Counteranion BF_4^- .

formed from a η^4 -cyclobutadiene complex, a solution of (1) and PhC_2Ph in CH_2Cl_2 was irradiated (u.v.) leading to the formation of (4) in high yield. This appears to be a general route to sterically crowded ruthenium arene cations⁶ since irradiation of (1) in the presence of PhC_2Me , MeC_2Me , or $\text{MeO}_2\text{CC}_2\text{CO}_2\text{Me}$ affords the cations (5), (6), and (7), respectively. A one step reaction between $[\text{Ru}(\text{CO})_2(\eta\text{-C}_5\text{H}_5)]_2$, an excess of EtC_2Et , and AgBF_4 using a nitrogen purge gave the hexaethylbenzene (heb) cation $[\text{Ru}(\eta^6\text{-C}_6\text{Et}_6)(\eta\text{-C}_5\text{H}_5)][\text{BF}_4]$ (8).

These observations are important from a synthetic standpoint, but also serve to refocus attention on the early idea that η^4 -cyclobutadiene complexes might serve as relay points on the path from alkynes to arenes, a reaction pathway which fell from favour with the publication of Whitesides' elegant labelling experiments.⁷ A plausible⁸ reaction pathway for the formation of, for example, (4), involves prior co-ordination of the alkyne, concomitant C-C and Ru-C bond formation, followed by reductive generation of the arene ring (Scheme 2).

The variable temperature n.m.r. spectrum of the heb cation (8) is particularly interesting in the context of the recent⁹⁻¹² controversy concerning restricted rotation about an arene-metal bond. A coalescence phenomenon is observed in the 100.61 MHz $^{13}\text{C}\text{-}\{^1\text{H}\}$ spectrum of (8) in $\text{CD}_2\text{Cl}_2\text{-CFCl}_3$. Although the $\eta\text{-C}_5\text{H}_5$ resonance is temperature invariant the

single contact arene ring resonance observed at room temperature collapses at 183 K to two singlets at δ 106.09 and 102.12. On further cooling to 173 K these signals broaden noticeably suggesting the presence of other isomers arising from slowed ethyl group rotation (ΔG_{205}^\ddagger 39.2 ± 1.2 kJ mol⁻¹). Finally at lower temperatures (163 to 143 K) the signals are observed to sharpen suggesting that only the most favoured (1,3,5-distal) isomer is present. This contrasts with the corresponding iron system where three heb stereoisomers (c, e, h)¹³ but not the 1,3,5-distal(a)¹³ (labelling as in original reference) are observed at 140 K. This difference presumably arises from the increased cyclopentadienyl-arene distance.

Finally, the ring expansion reaction observed with alkynes can be extended to alkenes. Irradiation of a solution of (1) in CH_2Cl_2 through which a stream of ethylene is bubbled affords an organic compound identified as 1,2,3,4-tetraphenylcyclohexa-1,3-diene and the pale yellow cation tris(ethylene)-(η -cyclopentadienyl)ruthenium tetrafluoroborate (9) (30% yield). The ^1H n.m.r. spectrum $[(\text{CD}_3)_2\text{CO}]$ of (9) is temperature invariant showing resonances at δ 5.73 (s, 5 H, C_5H_5), 3.84 (m, 6 H, C_2H_4), and 3.43 (m, 6 H, C_2H_4) [(AB)₂ system with $J(\text{AB})$ 0.64, $J(\text{AA}')$ 14.76, and $J(\text{AB}')$ 9.29 Hz].§ The

§ The assignment of the coupling constants was by computer simulation, for which we thank Dr. M. Murray.

^{13}C - $\{^1\text{H}\}$ spectrum $[(\text{CD}_3)_2\text{CO}]$ exhibited only two resonances at δ 90.28 (s, C_5H_5) and 59.0 (s, C_2H_4) showing that a plane of symmetry exists through each co-ordinated ethylene such that the two ends of the ethylene are chemically equivalent. This suggests that in solution the molecule adopts the illustrated tripodal arrangement where the three C_2H_4 ligands lie in a plane. This is an unusual reaction of co-ordinated η^4 -cyclobutadiene, and a stepwise process analogous to that assumed for the alkyne reaction is suggested affording a co-ordinated cyclohexa-1,3-diene, displacement with ethylene providing a route to the first trisethylene(η -cyclopentadienyl)metal complex.

We thank the S.E.R.C. for support, B.P. (Sunbury) for a CASE Studentship (M. C.), Dr. Philip Lodge (B.P.) and Dr. P. Woodward for encouragement, and Dr. B. E. Mann (Sheffield) for the 100.61 MHz ^{13}C n.m.r. spectra.

Received, 15th May 1984; Com. 677

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