The Synthesis, Structure, and Reactivity of Cationic η4-Cyclobutadiene–Ruthenium Complexes; Formation of the Trisethylene(η-cyclopentadienyl)ruthenium Cation

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Reaction of $[Ru(CO)_2(\eta\text{-}C_5H_5)]_2$ with $AgBF_4$ and PhC_2Ph affords $[Ru(CO)(\eta^4\text{-}C_4Ph_4)(\eta\text{-}C_5H_5)][BF_4]$, which on u.v. irradiation in MeCN gives $[Ru(NCMe)(\eta^4\text{-}C_4Ph_4)(\eta\text{-}C_5H_5)][BF_4]$ identified by X-ray crystallography; similar irradiation of the carbonyl cation in the presence of alkynes or ethylene gives the sterically hindered arene cations $[Ru(\eta^6\text{-arene})(\eta\text{-}C_5H_5)][BF_4]$ and $[Ru(\eta^2\text{-}C_2H_4)_3(\eta\text{-}C_5H_5)][BF_4]$.

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 $[Ru(CO)_2(\eta\text{-}C_5H_5)]_2$

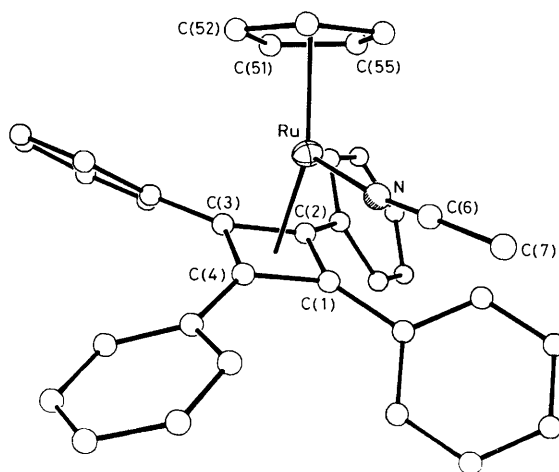**Figure 1.** Molecular structure of [Ru(MeCN)(η-C₄Ph₄)(η-C₅H₅)]⁺ (3) showing the atomic labelling scheme. Important geometric parameters include: lengths Ru–C(51) 2.191(3), Ru–C(52) 2.255(3), Ru–C(53) 2.237(3), Ru–C(54) 2.234(3), Ru–C(55) 2.246(3), Ru–N 2.070(2), N–C(6) 1.135(4), C(51)–C(52) 1.433(4), 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 CH₂Cl₂ leads to a redox reaction, and the formation of a separable mixture of [Ru(CO)(η⁴-C₄Ph₄)(η-C₅H₅)][BF₄] (1)† (47% yield), [Ru(CO)₂(η²-PhC₂Ph)(η-C₅H₅)][BF₄] (2), and [Ru(CO)₃(η-C₅H₅)][BF₄]. The remaining terminal carbonyl ligand in (1) is photolabile and u.v. irradiation in acetonitrile affords [Ru(NCMe)(η⁴-C₄Ph₄)(η-C₅H₅)][BF₄] (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
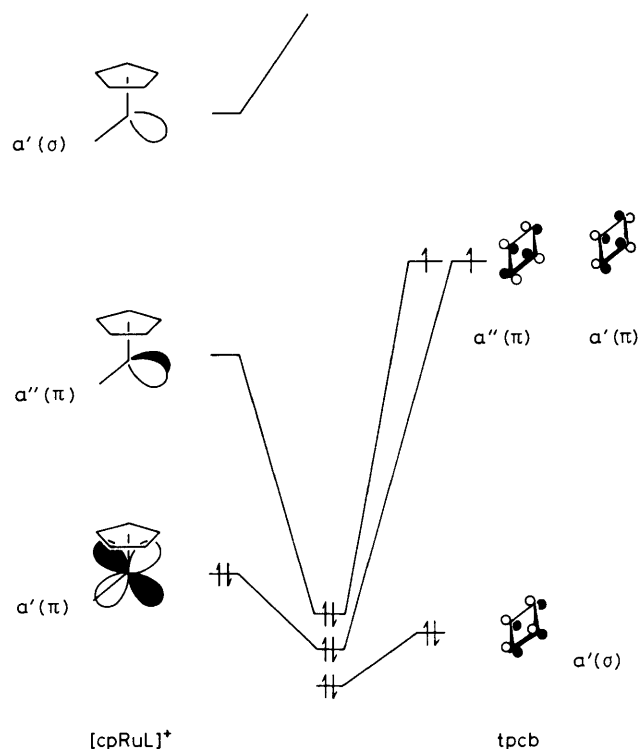
Scheme 1. Qualitative interaction diagram for d⁶-[cpRuL]⁺ and C₄R₄ fragments.
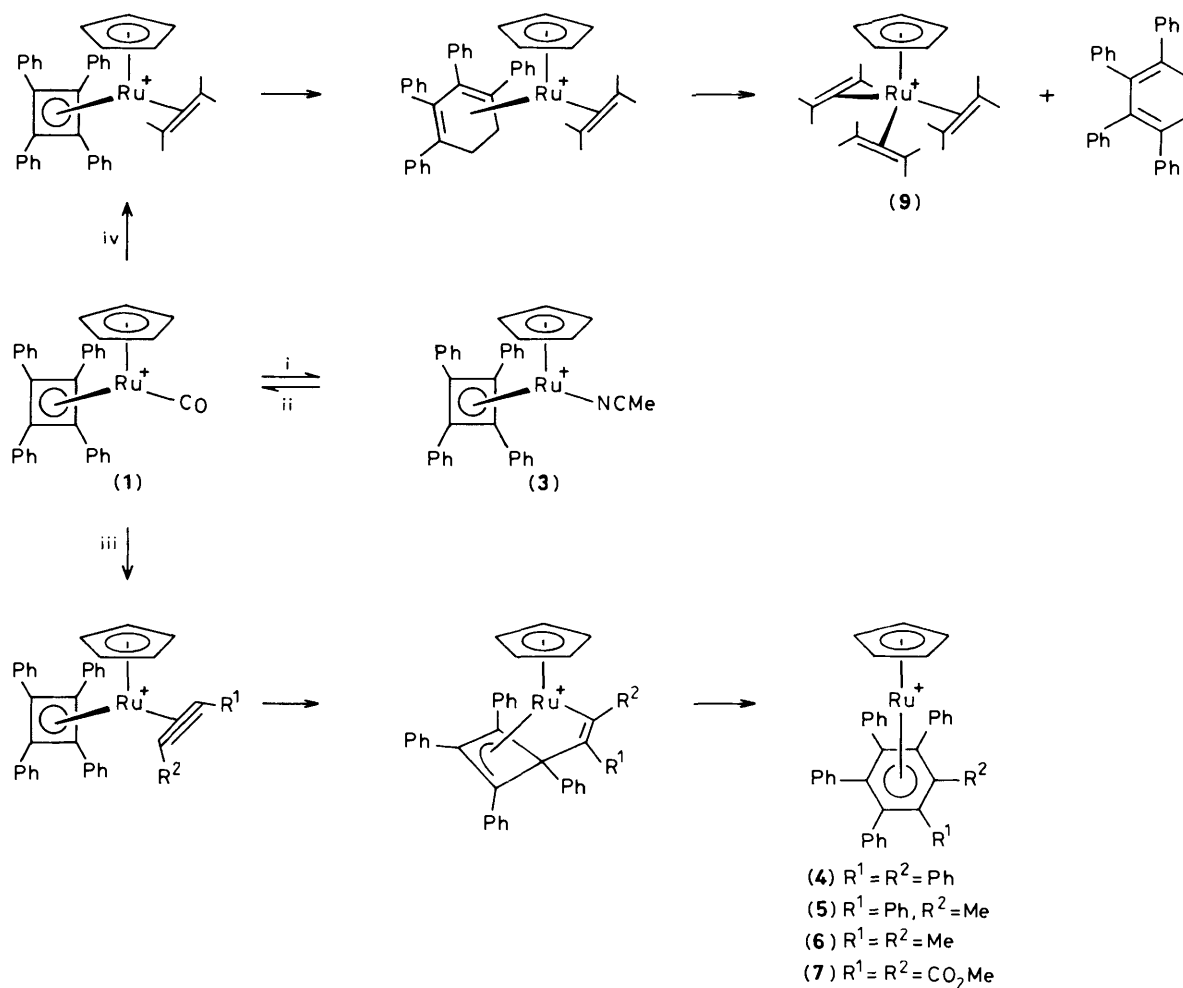
approximately symmetrical; Ru–C distances are 2.192(2), 2.208(3), 2.177(2), and 2.175(2) Å for C(1), C(2), C(3), and C(4), respectively. The C(1)–C(2) and C(3)–C(4) bonds lie nearly parallel to the Ru, N, tpcb, cp plane, deviating by 10.2 and 10.7°, respectively. The tpcb ring is markedly rectangular 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 d⁶-cpRuL⁺ fragment (see Scheme 1) which break the degeneracy of the e_g set of cyclobutadiene orbitals [e_g → a' + a" in the approximate C_s 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 e₁" orbitals.

[Ru(CO)₂(η²-PhC₂Ph)(η-C₅H₅)][BF₄]

(2)

[Ru(η⁶-C₆Et₆)(η-C₅H₅)][BF₄]

(8)
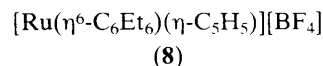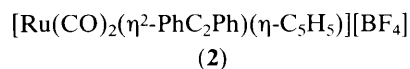
Recent studies⁵ on the reversibility of η⁴-cyclobutadiene–cobalt formation from complexed alkynes suggest that the immediate precursor of (1) is the bisalkyne cation [RU(CO)(η²-PhC₂Ph)₂(η-C₅H₅)]⁺ rather than a Ruᴵⱽ metallacyclopentadiene. However, an attempt to generate this intermediate by irradiating (u.v.) the monoalkyne cation (2) in the presence of PhC₂Ph led instead to the formation of the sterically crowded hexaphenylbenzene complex [Ru(η⁶-C₆Ph₆)(η-C₅H₅)][BF₄] (4). Suspecting that (4) might be

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 cations[6] since irradiation of (1) in the presence of PhC_2Me, MeC_2Me, or $MeO_2CC_2CO_2Me$ affords the cations (5), (6), and (7), respectively. A one step reaction between $[Ru(CO)_2(\eta-C_5H_5)]_2$, an excess of EtC_2Et, and $AgBF_4$ using a nitrogen purge gave the hexaethylbenzene (heb) cation $[Ru(\eta^6-C_6Et_6)(\eta-C_5H_5)][BF_4]$ (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 plausible[8] 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 recent[9—12] controversy concerning restricted rotation about an arene–metal bond. A coalescence phenomenon is observed in the 100.61 MHz ^{13}C-$\{^1H\}$ spectrum of (8) in CD_2Cl_2–$CFCl_3$. Although the η-C_5H_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 ($\Delta G^\ddagger_{205}$ 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-tetraphenyl-cyclohexa-1,3-diene and the pale yellow cation tris(ethylene)-(η-cyclopentadienyl)ruthenium tetrafluoroborate (9) (30% yield). The ^1H n.m.r. spectrum [$(CD_3)_2CO$] of (9) is temperate 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 $J(AB)$ 0.64, $J(AA')$ 14.76, and $J(AB')$ 9.29 Hz].§ The

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

^{13}C-$\{^{1}H\}$ spectrum [$(CD_3)_2CO$] 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.

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