

**Conversion of Bonded Cyclo-octadiene into a Cyclo-octadienyl Ligand and
Cleavage of Boron-Phenyl Bonds of Arene-bonded Tetraphenylborate
Anions in Ruthenium(II) Systems: X-Ray Crystal and Molecular
Structures of $[\text{Ru}(\eta^6\text{-C}_6\text{H}_5\text{BL}_3)(1\text{---}3,5,6\text{-}\eta\text{-C}_8\text{H}_{11})]$ ($\text{L} = \text{Ph}$ or F)**

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Summary Labilisation of the hydrazine ligands in either $[\text{Ru}(\text{cod})(\text{N}_2\text{H}_4)_4][\text{BPh}_4]_2$ (I; cod = cyclo-octa-1,5-diene) or $[\text{RuH}(\text{cod})(\text{NH}_2\text{NMe}_2)_3][\text{BPh}_4]$ (II) in acetone produces $[\text{Ru}(\eta^6\text{-C}_6\text{H}_5\text{BPh}_3)(1\text{---}3,5,6\text{-}\eta\text{-C}_8\text{H}_{11})]$ which reacts with HA ($\text{A} = \text{BF}_4$ or PF_6) to give $[\text{Ru}(\eta^6\text{-C}_6\text{H}_5\text{-BF}_3)(1\text{---}3,5,6\text{-}\eta\text{-C}_8\text{H}_{11})]$; a byproduct of the reaction with (II) is $[\text{Ru}(\text{cod})(\text{C}_6\text{H}_6)]$.

We have recently shown¹ that the hydrazine ligands in $[\text{Ru}(\text{cod})(\text{N}_2\text{H}_4)_4][\text{BPh}_4]_2$ (I) and $[\text{RuH}(\text{cod})(\text{NH}_2\text{NMe}_2)_3][\text{A}]$ (II; $\text{A} = \text{PF}_6$ or BPh_4) (cod = cyclo-octa-1,5-diene) undergo easy replacement with donor ligands in methanol to give highly reactive cationic ruthenium(II) systems. We

now find that simply refluxing (I) in acetone-ethanol mixtures effects its conversion into the highly insoluble π -allyl-ruthenium(II) complex $[\text{Ru}(\eta^6\text{-C}_6\text{H}_5\text{BPh}_3)(1\text{---}3,5,6\text{-}\eta\text{-C}_8\text{H}_{11})]$ (III). When (II; $\text{A} = \text{BPh}_4$) was used, a competing reaction was observed producing (III) (16%) and the known² ruthenium(0) compound $[\text{Ru}(\text{cod})(\text{C}_6\text{H}_6)]$ (IV; 50%). Addition of benzene to the refluxing solution of (II) in acetone gave (IV) in 70% yield.

The formulation for (III) has been confirmed by an X-ray structural determination (Figure 1). The conversion of a cyclo-octadiene ligand of a ruthenium(II) complex into a π -allyl-olefin ligand is unprecedented, although similar reactions of olefin ligands are well known for ruthenium(0)

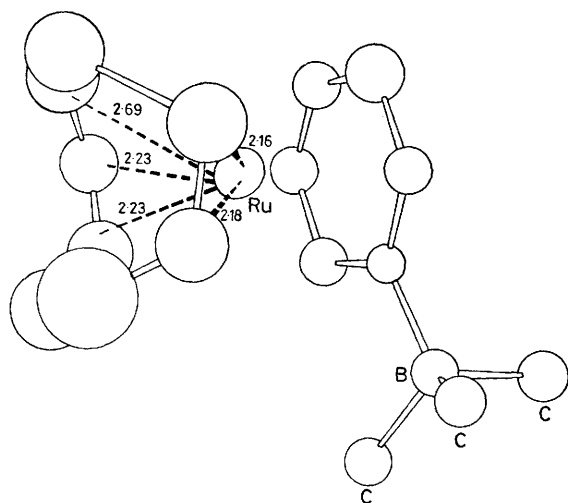
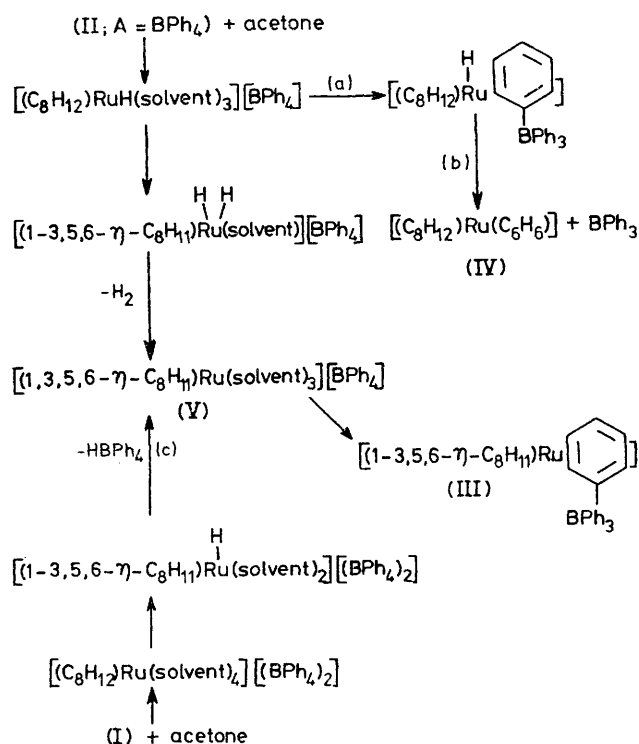


FIGURE 1. The structure of $[\text{Ru}(\eta^6\text{-C}_6\text{H}_5\text{BPh}_3)(1\text{-}3,5,6\text{-}\eta\text{-C}_8\text{H}_{11})]$ (III).

complexes, *e.g.* in the reaction of $[\text{Ru}_3(\text{CO})_{12}]$ with cyclo-dodecatriene³ and in the suggested mechanism for the catalytic isomerization of cod by $[\text{Ru}(\text{cod})(\text{CO})_3]$.⁴

The formation of (IV) under the above conditions is also significant for two reasons: (i) a reduction of ruthenium(II) to ruthenium(0) occurs under unusually mild conditions and (ii) a new type of metal arylation and reduction by a tetraphenylborate anion is observed. We are at present investigating the formation of the complexes *via* possible reaction pathways involving the steps shown in the Scheme.



SCHEME

† The chemical shifts were measured with respect to $^{13}\text{CD}_3\text{NO}_2$ (59.40 p.p.m.) and are quoted with respect to internal Me_4Si . Increasing frequency is taken as positive.

It is feasible that the reduction to ruthenium(0) in steps (a) and (b) (Scheme) may in fact occur by reductive elimination of benzene from a ruthenium-hydrido- η^1 -aryl intermediate generated by cleavage⁵ of a boron-carbon bond in BPh_4^- . Evidence for the possible intermediate (V) in the formation of (III) came from the reactions of (I) with cyclo-octatetraene (cot) and cycloheptatriene (cht) which gave $[(1\text{-}3,5,6\text{-}\eta\text{-C}_8\text{H}_{11})\text{RuL}]^+$ (VI; L = cot or cht). In addition, use of $[\text{Ru}(\text{cod})(\text{NH}_2\text{NHMe})_4][\text{PF}_6]_2$ instead of (I) also gave (VI; L = cot or cht), and we are presently investigating the suitability of this salt as a precursor to cationic π -allylic ruthenium(II) complexes.

Attempts to reverse step (c) by treating (III) with HPF_6 or HBF_4 in MeCN produced a pale yellow complex which analysed satisfactorily for $\text{RuC}_{14}\text{H}_{16}\text{BF}_3$ (VII). Similar reactions of (III) with HF also gave (VI); it is therefore possible that the fluorination occurs with HF generated in the equilibrium $\text{HBF}_4 \rightleftharpoons \text{HF} + \text{BF}_3$ or $\text{HPF}_6 \rightleftharpoons \text{HF} + \text{PF}_5$. Because of the novelty of this reaction, the structure of (VII) was determined from 3-dimensional X-ray crystallographic data and shown to be $[\text{Ru}(\eta^6\text{-C}_6\text{H}_5\text{BF}_3)(1\text{-}3,5,6\text{-}\eta\text{-C}_8\text{H}_{11})]$ (Figure 2). The ^{13}C n.m.r. spectrum of (VII) in

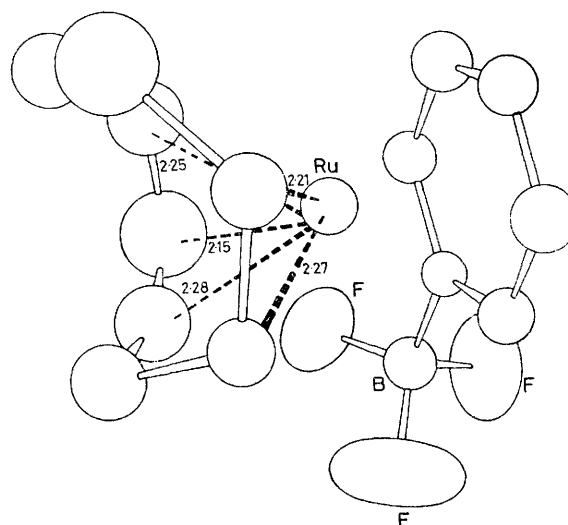


FIGURE 2. The structure of $[\text{Ru}(\eta^6\text{-C}_6\text{H}_5\text{BF}_3)(1\text{-}3,5,6\text{-}\eta\text{-C}_8\text{H}_{11})]$ (VII).

CD_3NO_2 solution shows three $^{-13}\text{CH}_2\text{-}$ resonances† at δ 17.36, 26.25, and 33.64 p.p.m. Resonances corresponding to $^{-13}\text{CH-}$ groups appear at δ 24.57, 29.61, 69.58, 77.31, and 80.69 p.p.m. and four other resonances which appear to be complicated by $J_{\text{C-F}}$ coupling are observed at δ 88.56, 89.58, 92.20, and 92.94 p.p.m. The ^1H n.m.r. spectrum of (VII) is extremely complex with the arene protons resonating at *ca.* τ 4 and the remaining protons appearing as a series of multiplets between τ 5 and 9. This is apparently due to coupling of the fluorine atoms on the $\eta^6\text{-C}_6\text{H}_5\text{BF}_3$ ligand with the protons of the cyclo-octadienyl ring. In contrast to the extreme insolubility of (III), (VII) is readily soluble, and is thus useful for the study of further reactions of arene-bonded cyclo-octadienyl ruthenium(II) complexes.

TABLE. Crystal data of complexes (III) and (VII).

		(III)	(VII)
<i>a</i> /Å	23.94(2)	12.04(2)
<i>b</i> /Å	10.58(2)	8.93(2)
<i>c</i> /Å	9.71(2)	12.07(2)
α /°	90.6(1)	
β /°	92.0(1)	
γ /°	93.0(1)	
<i>Z</i>	4	4
System		Triclinic	Orthorhombic
Space group	..	$P\bar{1}$	$Pna2_1$
<i>D_c</i> /g cm ⁻³	..	1.43	1.81
<i>D_m</i> /g cm ⁻³	..	1.42	1.81
No. of reflections		4561	1345
θ -range/°	..	3—20	3—25
<i>R</i>	0.095	0.076

Intensity data were collected on the Philips four-circle diffractometer at the N.P.R.L., C.S.I.R., by the ω - 2θ scan technique using graphite monochromatized Mo- K_α radiation.

The structures were solved by Patterson and Fourier methods and were refined by full-matrix least-squares refinement. Crystals of (III) contained two molecules in the asymmetric unit, one of which is shown in Figure 1 with relevant bond lengths. Crystal data for complexes (III) and (VII) are given in the Table.†

Although in each structure certain co-ordinates of the carbon atoms of the C₈ rings are of low accuracy at this stage, their conformation, and the presence of five ring carbon atoms within bonding distance of ruthenium unequivocally show the presence of a 1—3,5,6- η -cyclo-octadienyl ligand. Both the η^6 -C₈H₅BPh₃ and η^6 -C₈H₅BF₃ ligands are well resolved.

We are indebted to Dr. A. A. Chalmers of this laboratory for determining the ¹³C n.m.r. spectrum of compound (VII).

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

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