Arene Ruthenium(II) Complexes formed by Dehydrogenation of Cyclohexadienes with Ruthenium(III) Trichloride

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Arenedi-μ-chloro-ruthenium complexes $[RuCl_2(arene)]_2$ have been prepared by dehydrogenation of the appropriate cyclohexa-1,3-diene or cyclohexa-1,4-diene with ethanolic ruthenium(III) trichloride. They react with ligands (L) such as pyridine, tertiary phosphines, or tertiary arsines to give monomeric complexes $[RuCl_2(arene)L]$, which are formally analogous to the arenetricarbonylchromium complexes. Analogous dibromo-, di-iodo-, halogeno(methyl), and dimethyl derivatives have also been prepared; the latter are thermally unstable and air-sensitive. Reaction of the complexes $[RuCl_2(arene)]_2$ (arene = benzene or *p*-cymene) with water gives binuclear tri-μ-chloro-cationic species $[Ru_2Cl_3(arene)_2]^+$, and reaction with silver(I) tetrafluoroborate in acetonitrile gives monomeric $[Ru(arene)(MeCN)_3]^{2+}$. I.r. and n.m.r. data for the new complexes are given. The complexes $[RuCl_2(arene)L]$ (L = PBu^n_3 or PPh_3) undergo partial or complete arene exchange on heating or on u.v. irradiation in an aromatic solvent, co-ordinated *p*-cymene being the most easily displaced. The exchange method can be used to prepare hexamethylbenzene complexes, *e.g.* $[RuCl_2(C_6Me_6)(PBu^n_3)]$. The results are compared with available data on arene exchange in arenetricarbonylchromium complexes and discussed in terms of electronic and steric effects on metal–arene bonding.

THE reaction of cyclohexa-1,3-diene with ethanolic ruthenium(III) trichloride was reported by Winkhaus and Singer [1] to give a brown, diamagnetic, insoluble benzene complex of empirical formula $[RuCl_2(C_6H_6)]$ which, on reaction with tri-*n*-butylphosphine, gave a red adduct $[RuCl_2(C_6H_6)(PBu^n_3)]$. This complex was stated to be dimeric in freezing bromoform, and on this basis a polymeric, chloro-bridged structure containing η^4-benzene and octahedrally co-ordinated ruthenium(II) was proposed for $[RuCl_2(C_6H_6)]$, analogous to those proposed for the polymeric complexes $[RuCl_2(diene)]_n$ (diene = norbornadiene or cyclo-octa-1,5-diene).[2] A red, crystalline complex $[RuCl_2(C_6H_6)(dmso)]$ obtained from $[RuCl_2(C_6H_6)]$ in dimethyl sulphoxide, and a hydrido-complex $[Ru(H)Cl(C_6H_6)(dmso)]$ have also been assumed [3] to be dimeric by analogy with the earlier work. Zelonka and Baird [4] and we [5] have reported in preliminary notes that a wide range of complexes $[RuCl_2(arene)L]$ (L = tertiary phosphine, phosphite, or arsine) can be made, and that they are monomeric in solution. Single-crystal *X*-ray studies [5] of two of these complexes, $[RuCl_2(C_6H_6)(PMePh_2)]$ and $[RuCl_2(p\text{-}MeC_6H_4CHMe_2)(PMePh_2)]$, have shown that they have a half-sandwich structure similar to that adopted by arenetricarbonylchromium complexes, except that in the ruthenium complexes the arene ring is slightly, but significantly, non-planar. We now describe our work in detail, and compare it, where appropriate, with the results of Zelonka and Baird,[6,7] which appeared during the preparation of this report.

RESULTS AND DISCUSSION

Preparation and Structure.—A series of arene complexes $[RuX_2(arene)]_2$ (X = Cl or Br; arene = C_6H_6, PhMe, $p\text{-}C_6H_4Me_2$, $1,3,5\text{-}C_6H_3Me_3$, or $p\text{-}MeC_6H_4CHMe_2$) was obtained by heating an ethanolic solution of ruthenium(III) trichloride with the corresponding cyclohexa-1,3-diene or cyclohexa-1,4-diene, the latter being readily accessible from the arene by metal–ammonia reduction. The *p*-cymene complex was obtained using commercially available α-phellandrene (5-isopropyl-2-methylcyclohexa-1,3-diene), which contained some α-terpinene (1-isopropyl-4-methylcyclohexa-1,3-diene). Yields varied from almost quantitative for $[RuCl_2(C_6H_6)]_2$ to only 6% for the *p*-xylene complex. There was no reaction between ethanolic $RuCl_3$ and cyclohexa-1,4-diene at room temperature, whereas with cyclohexa-1,3-diene under identical conditions the complex $[RuCl_2(C_6H_6)]_2$ was precipitated over a period of days. This suggests that the 1,4-dienes may isomerise to the 1,3-dienes before dehydrogenation takes place. The anisole complex $[RuCl_2(C_6H_5OMe)]_2$ can be made from 1-methoxycyclohexa-1,4-diene and methanolic $RuCl_3$. Use of ethanolic $RuCl_3$ gave an as yet unidentified complex which contained an ethyl, but no methyl group. Some demethoxylation occurred in the reaction with methanolic $RuCl_3$, since n.m.r. evidence suggested that *ca.* 10% of the benzene complex is formed in addition to the anisole complex.

The iodo-complex $[RuI_2(C_6H_6)]_2$ was obtained from the reaction of ethanolic ruthenium(III) trichloride and an excess of sodium iodide with cyclohexa-1,3-diene, but the corresponding bromo-complex could not be obtained by using an excess of sodium bromide (see below); it is necessary to start with ruthenium(III) tribromide, or, as shown by Zelonka and Baird,[6] to carry out the reaction of the complex $[RuCl_2(C_6H_6)]_2$ with sodium bromide in water.

The complexes $[RuCl_2(arene)]_2$ are brown, diamagnetic, and poorly soluble in most organic solvents except

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[1] G. Winkhaus and H. Singer, *J. Organometallic Chem.*, 1967, **7**, 487.

[2] E. W. Abel, M. A. Bennett, and G. Wilkinson, *J. Chem. Soc.*, 1959, 3178; M. A. Bennett and G. Wilkinson, *Chem. and Ind.*, 1959, 1516.

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[4] R. A. Zelonka and M. C. Baird, *J. Organometallic Chem.*, 1972, **35**, C43.

[5] M. A. Bennett, G. B. Robertson, and A. K. Smith, *J. Organometallic Chem.*, 1972, **43**, C41.

[6] R. A. Zelonka and M. C. Baird, *Canad. J. Chem.*, 1972, **50**, 3063.

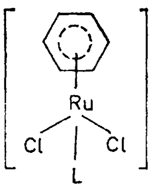
[7] R. A. Zelonka and M. C. Baird, *J. Organometallic Chem.*, 1972, **44**, 383.

TABLE 1

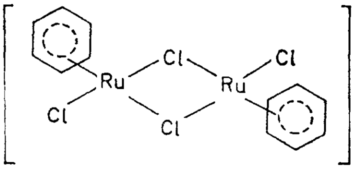
Analytical data (%), molecular weights, melting points, and Ru–Cl stretching wavenumbers (cm^{-1}) for arene ruthenium complexes

Complex	M.p. (t/°C)	Analyses: found (calc.) C	H	X	P	M: found (calc.)	ν(RuCl)
$[RuCl_2(C_6H_6)]_2$	242	28·9(28·8)	2·8(2·4)	28·2(28·3)			295, 259, 248sh
$[RuBr_2(C_6H_6)]_2$	>250	20·4(21·3)	1·9(1·8)	47·9(47·1)			
$[RuI_2(C_6H_6)]_2$	255	17·2(16·6)	1·6(1·4)	57·3(58·6)			
$[RuCl_2(C_6H_5Me)]_2$	>250	31·1(31·8)	3·3(3·1)	27·4(26·9)			293, 250br
$[RuCl_2(p\text{-}C_6H_4Me_2)]_2$	230	34·3(34·55)	3·5(3·6)				292, 254, 247sh
$[RuCl_2(1,3,5\text{-}C_6H_3Me_3)]_2$	296	36·7(37·0)	4·1(4·1)	24·3(24·3)			298 270, 260, 248sh
$[RuCl_2(p\text{-}MeC_6H_4CHMe_2)]_2$	200	38·4(39·2)	4·7(4·6)	23·3(23·2)		604(612)	292, 260, 250sh
$[RuCl_2(C_6H_5OMe)]_2$	235	28·7(30·0)	2·8(2·9)	24·8(25·3)			300, 255, 248sh
$[RuCl_2(C_6H_6)(PBu^n_3)]$	197—200	48·1(47·8)	7·3(7·35)	15·6(15·7)	7·1(6·8)	448(452)	287, 269
$[RuBr_2(C_6H_6)(PBu^n_3)]$	199	39·9(39·9)	5·9(6·1)	29·9(29·5)	6·2(5·7)		
$[RuI_2(C_6H_6)(PBu^n_3)]$	n.m.	36·0(34·0)	5·6(5·2)				
$[RuCl_2(C_6H_6)\{P(octyl)_3\}]$	162—164	57·7(58·05)	9·4(9·3)		4·9(5·0)		290, 270
$[RuCl_2(C_6H_6)(PMe_2Ph)]$	174—177	44·5(43·3)	4·8(4·4)		8·4(8·0)	422(388)	290, 280
$[RuI_2(C_6H_6)(PMe_2Ph)]$	197	29·5(29·4)	3·1(3·0)	44·4(44·4)		553(571)	
$[RuCl_2(C_6H_6)(PMePh_2)]$	195	50·2(50·7)	4·4(4·2)	16·3(15·8)	6·7(6·9)		291, 278br
$[RuBr_2(C_6H_6)(PMePh_2)]$	212	42·0(42·3)	3·7(3·55)	30·7(29·6)			
$[RuCl_2(C_6H_6)(PPh_3)]$	184	56·1(56·3)	4·2(4·1)	14·0(13·8)	6·15(6·05)	544(539)	292, 280
$[RuCl_2(C_6H_6)\{P(OMe)_3\}]$	darkens >160	28·5(28·9)	4·1(4·0)		7·8(8·3)	377(374)	291, 280
$[RuCl_2(C_6H_6)(AsMe_3)]$	204	28·9(29·4)	4·4(4·1)			396(371)	287, 275
$[RuCl_2(C_6H_6)(AsMe_2Ph)]$	190	39·1(38·9)	4·0(4·0)	16·6(16·4)			295, 278
$[RuCl_2(C_6H_5Me)(PBu^n_3)]$	191	49·3(48·9)	7·4(7·6)	15·4(15·2)	6·5(6·6)	448(466)	295, 279
$[RuCl_2(m\text{-}C_6H_4Me_2)(PBu^n_3)]$	180	50·0(50·0)	7·7(7·8)		6·15(6·45)	455(480)	n.m.
$[RuCl_2(p\text{-}C_6H_4Me_2)(PMePh_2)]$	175	52·8(52·7)	4·9(4·85)			465(478)	289, 280
$[RuCl_2(1,3,5\text{-}C_6H_3Me_3)(PMe_2Ph)]$	187 decomp.	47·2(47·45)	5·4(5·4)	16·9(16·5)	7·5(7·2)	429(430)	294, 280
$[RuCl_2(1,3,5\text{-}C_6H_3Me_3)(py)]$	296 [a]	45·0(45·3)	5·1(4·6)	18·9(19·1)	3·6(3·8) [b]		292, 284
$[RuCl_2(C_6Me_6)(PBu^n_3)]$	170	53·6(53·7)	8·2(8·45)	13·4(13·2)	5·4(5·8)	511(537)	301, 292
$[RuCl_2(p\text{-}MeC_6H_4CHMe_2)(PBu^n_3)]$	162—166	52·75(53·5)	8·4(8·1)	14·4(14·0)	6·0(6·1)	493(508)	291, 284
$[RuCl_2(p\text{-}MeC_6H_4CHMe_2)(PMe_2Ph)]$	180	48·6(48·7)	5·5(5·6)	15·8(16·0)	7·1(7·0)		293, 284sh
$[RuCl_2(p\text{-}MeC_6H_4CHMe_2)(PMePh_2)]$	178—181	54·3(54·6)	5·4(5·3)	13·7(14·0)	6·3(6·1)	507(506)	295, 285
$[RuCl_2(p\text{-}MeC_6H_4CHMe_2)(PPh_3)]$	170	59·3(59·1)	5·1(5·1)		5·4(5·45)	539(569)	290, 281
$[RuCl_2(p\text{-}MeC_6H_4CHMe_2)(AsMe_2Ph)]$	183—186	44·0(44·3)	5·2(5·2)	14·4(14·5)			285br
$[RuCl_2(p\text{-}MeC_6H_4CHMe_2)(py)]$	179—182	47·1(46·8)	5·1(5·0)	18·4(18·4)		383(385)	291, 285
$[RuCl_2(C_6H_5OMe)(PMePh_2)]$	168	49·8(49·0)	4·5(3·9)			456(465)	293, 282
$[Ru_2Cl_3(C_6H_6)_2]PF_6$	245	24·3(23·6)	2·0(2·0)	15·8(17·4)	3·9(5·0)		265br
$[Ru_2Cl_3(p\text{-}MeC_6H_4CHMe_2)_2]PF_6$	238	34·0(33·3)	4·0(3·9)	13·6(14·7)	3·2(4·3)		260br
$[Ru(C_6H_6)(MeCN)_3](BF_4)_2$	darkens >150	29·8(30·3)	3·2(3·2)	31·75(31·9)	8·5(8·8) [b]		2 330, 2 300 [c]
$[Ru(I)Me(C_6H_6)(PMe_2Ph)]$	138	39·1(39·2)	4·5(4·4)	27·7(27·6)			
$[RuMe_2(1,3,5\text{-}C_6H_3Me_3)(PMe_2Ph)]$	decomp. r.t.	58·9(58·6)	7·7(7·5)				

[a] Loses pyridine before melting. [b] Nitrogen analysis. [c] ν(CN) (Nujol).



(I)



(II)

dmso. The p-cymene complex was sufficiently soluble in chloroform for an osmometric determination of molecular weight, which showed the complex to be dimeric, and we assume this to be true for the other arene complexes. We suggest the chloro-bridged structure (II) containing η^6-arene, which is obviously similar to that of the dimeric isoelectronic pentamethylcyclopentadienyl complexes $[MCl_2(C_5Me_5)]_2$ (M = Rh or Ir).[8] The far i.r. spectra of the $[RuCl_2(arene)]_2$ complexes (Table 1) showed two strong bands in the region of **290** and **250** cm^{-1} assignable to ν(RuCl) modes of terminal and bridging chlorine atoms, and the i.r. spectrum of the complex $[RuCl_2(C_6H_6)]_2$ reported by Winkhaus and Singer[1] is clearly compatible with η^6-C_6H_6 by comparison with the spectra of $Cr(C_6H_6)_2$ and $[Cr(CO)_3(C_6H_6)]$. The proton n.m.r. spectra of the benzene complexes in $[^2H_6]$dmso, in which monomers $[RuX_2(C_6H_6)(dmso)]$ are undoubtedly present, showed sharp singlets (Table 2) due to co-ordinated η^6-benzene, which were characteristically *ca.* 2·0 p.p.m. upfield of the free benzene resonance. Similar upfield shifts were observed for the aromatic proton resonances of the other arenes in their Ru^{II} complexes. We have no evidence to suggest that our sample of $[RuCl_2(C_6H_6)]_2$ differs in solubility or other properties from that origin-

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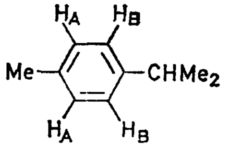
[8] J. W. Kang, K. Moseley, and P. M. Maitlis, *J. Amer. Chem. Soc.*, 1969, **91**, 5970.

TABLE 2

N.m.r. data for arene ruthenium(II) complexes [a,b]

Compound	Co-ordinated arene protons	Others
$[RuCl_2(C_6H_6)]_2$ [c]	4·02(s)	
$[RuBr_2(C_6H_6)]_2$ [c]	3·96(s)	
$[RuI_2(C_6H_6)]_2$ [c]	3·90(s)	
$[RuCl_2(PhMe)]_2$ [c]	4·02(m), 4·31(m), 7·84(s, CH_3)	
$[RuCl_2(p\text{-}C_6H_4Me_2)]_2$	4·75(s), 7·83(s, CH_3)	
$[RuCl_2(1,3,5\text{-}C_6H_3Me_3)]_2$ [c]	4·50(s), 7·84(s, CH_3)	
$[RuCl_2(p\text{-}MeC_6H_4CHMe_2)]_2$ [d]	4·60, 4·72($\mathrm{H_A,H_B}$, J 6), 7·12(sp, $CHCH_3$), 7·87(s, CH_3), 8·74(d, $CHCH_3$, J 7)	
$[RuCl_2(C_6H_5OMe)]_2$ [c]	3·79(t), 4·42(d), 4·58(t), [e] 6·05(s, CH_3)	
$[RuCl_2(C_6H_6)(PBu^n_3)]$	4·42[d, J(P–H) 0·8]	7·98(m), 8·54(m), 9·06(m) (n-butyl)
$[RuBr_2(C_6H_6)(PBu^n_3)]$	4·37[d, J(P–H) 0·9]	7·90(m), 8·54(m), 9·04(m) (n-butyl)
$[RuI_2(C_6H_6)(PBu^n_3)]$	4·28[d, J(P–H) 0·75]	7·81(m), 8·54(m), 9·05(m) (n-butyl)
$[RuCl_2(C_6H_6)\{P(octyl)_3\}]$	4·44(s) [f]	7·98(m), 8·65(m), 9·10(m) (n-octyl)
$[RuCl_2(C_6H_6)(PMe_2Ph)]$	4·64[d, J(P–H) 0·8]	2·50(m, Ph), 8·13[d, CH_3, J(P–H) 11·5]
$[RuCl_2(C_6H_6)(PMePh_2)]$	4·60[d, J(P–H) 0·8]	2·34(m, Ph), 8·05[d, CH_3, J(P–H) 12]
$[RuBr_2(C_6H_6)(PMePh_2)]$	4·54[d, J(P–H) 0·8]	2·32(m, Ph), 7·85[d, CH_3, J(P–H) 11]
$[RuCl_2(C_6H_6)(PPh_3)]$	4·62[d, J(P–H) 0·45]	2·45(m, Ph)
$[RuCl_2(C_6H_6)\{P(OMe)_3\}]$	4·26[d, J(P–H) 0·5]	6·17[d, CH_3, J(P–H) 11]
$[RuCl_2(C_6H_6)(AsMe_3)]$	4·39(s)	8·44(s, CH_3)
$[RuCl_2(C_6H_6)(AsMe_2Ph)]$	4·54(s)	2·37(m, Ph), 8·27(s, CH_3)
$[RuCl_2(PhMe)(PBu^n_3)]$	4·40—5·04(m), 7·74(s, CH_3)	8·00(m), 8·55(m), 9·04(m) (n-butyl)
$[RuCl_2(p\text{-}C_6H_4Me_2)(PMePh_2)]$	4·83[d, J(P–H) 1·1), 8·18(s, CH_3)	2·36(m, Ph), 8·08[d, CH_3, J(P–H) 11·5]
$[RuCl_2(1,3,5\text{-}C_6H_3Me_3)(PMe_2Ph)]$	5·28(s), 8·04(s, CH_3)	2·0—2·7(m, Ph), 8·23[d, CH_3, J(P–H) 11]
$[RuCl_2(1,3,5\text{-}C_6H_3Me_3)(py)]$	5·12(s), 7·96(s, CH_3)	0·95(m), 2·2—2·8(m) (pyridine)
$[RuCl_2(PhCHMe_2)(PBu^n_3)]$	4·62(m), 6·93(t, $CHMe_2$), 8·75(d, CH_3 of $CHMe_2$, J 7·0)	8·0(m), 8·55(m), 9·05(m) (n-butyl)
$[RuCl_2(p\text{-}MeC_6H_4CHMe_2)(PBu^n_3)]$ [d]	4·58(s, H_A,H_B), 7·18(sp, $CHMe_2$), 8·75(d, CH_3 of $CHMe_2$, J 7·0), 7·92(s, CH_3)	8·02(m), 8·57(m), 9·06(m) (n-butyl)
$[RuBr_2(p\text{-}MeC_6H_4CHMe_2)(PBu^n_3)]$	4·52(s, H_A,H_B), 6·98(sp, $CHMe_2$), 8·74(d, CH_3 of $CHMe_2$, J 7·0), 7·82(s, CH_3)	7·93(m), 8·56(m), 9·05(m) (n-butyl)
$[RuI_2(p\text{-}MeC_6H_4CHMe_2)(PBu^n_3)]$	4·50(s, H_A,H_B), 6·70(sp, $CHMe_2$), 8·70(d, CH_3 of $CHMe_2$, J 7·0), 7·64(s, CH_3)	7·82(m), 8·53(m), 9·04(m) (n-butyl)
$[RuCl_2(p\text{-}MeC_6H_4CHMe_2)(PMe_2Ph)]$	4·82(s, H_A,H_B), 7·38(sp, $CHMe_2$), 8·90(d, CH_3 of $CHMe_2$, J 7·0), 8·18(s, CH_3)	2·36(m, Ph), 8·16[d, CH_3, J(P–H) 11]
$[RuCl_2(p\text{-}MeC_6H_4CHMe_2)(PMePh_2)]$ [d]	4·70, 4·81(H_A,H_B, J 6), 7·48(sp, $CHMe_2$), 9·10(d, CH_3 of $CHMe_2$, J 7·0), 8·09(s, CH_3)	2·38(m, Ph), 8·11[d, CH_3, J(P–H) 11·5]
$[RuCl_2(p\text{-}MeC_6H_4CHMe_2)(PPh_3)]$ [d]	4·84, 5·03(H_A,H_B, J 6), 7·18(sp, $CHMe_2$), 8·90(d, CH_3 of $CHMe_2$, J 7·0), 8·13(s, CH_3)	2·48(m, Ph)
$[RuCl_2(p\text{-}MeC_6H_4CHMe_2)(AsMe_2Ph)]$	4·71(s, H_A,H_B), 7·27(sp, $CHMe_2$), 8·85 (d, CH_3 of $CHMe_2$, J 7·0), 8·04(s, CH_3)	2·42(m, Ph), 8·30(s, CH_3)
$[RuCl_2(p\text{-}MeC_6H_4CHMe_2)(py)]$ [d]	4·57, 4·78(H_A,H_B, J 6), 7·02(sp, $CHMe_2$), 8·69(d, CH_3 of $CHMe_2$, J 7·0), 7·91(s, CH_3)	0·95(m), 1·29(m), 1·70(m) (pyridine)
$[RuCl_2(C_6H_5OMe)(PMePh_2)]$	4·49(m), 4·99(d), 5·83(d), 6·10(s, CH_3) [g]	2·38(m, Ph), 8·03[d, CH_3, J(P–H) 11·5]
$[RuCl_2(C_6Me_6)(PBu^n_3)]$	7·99(s, CH_3 of C_6Me_6)	8·1(m), 8·65(m), 9·1(m) (n-butyl)
$[Ru(Cl)Me(C_6H_6)(PMe_2Ph)]$	5·37(s) [f]	2·68(m, Ph), 8·30(d, P–Me, J 10), 8·58[d, Ru-Me, J(P–H) 8], 8·75(d, P-Me, J 10)
$[Ru(I)Me(C_6H_6)(PMe_2Ph)]$	5·25[d, J(P–H) 0·9]	2·44(m, Ph), 8·17(d, P–Me, J 10·5), 8·57[d, Ru–Me, J(P–H) 8], 8·67(d, P–Me, J 10·5)
$[RuMe_2(C_6H_6)(PMe_2Ph)]$	5·39(s) [f]	2·72(m, Ph), 8·74(d, P–Me, J 8·5), 9·49[d, Ru–Me, J 7]
$[RuMe_2(1,3,5\text{-}C_6H_3Me_3)(PMe_2Ph)]$	5·78(s), [f] 8·33(s, CH_3)	2·3—2·9(m, Ph), 8·72(d, P–Me, J 8·5), 9·63[d, Ru–Me, J(P–H) 6·5]
$[Ru(Cl)Me(C_6H_6)(PPh_3)]$	4·78(s) [f]	2·6—3·0(m, Ph), 8·76[d, Ru–Me, J(P–H) 8]
$[RuMe_2(C_6H_6)(PPh_3)]$	5·05(s) [f]	2·6—3·0(m, Ph), 9·93[d, Ru–Me, J(P–H) 6·5]
$[RuMe_2(C_6H_6)(PBu^n_3)]$	4·70(s) [f]	8·05(m), 8·53(m), *ca.* 9·0(m) (n-butyl, partially overlapping Ru–Me), 8·95[d, Ru–Me, J(P–H) 7]

[a] Measured in $CDCl_3$ at *ca.* 34 °C except where stated otherwise; chemical shifts (τ) relative to $SiMe_4$ as internal standard, J in Hz. [b] Abbreviations: s, singlet; d, doublet; sp, septet; t, triplet; m, multiplet. [c] Measured in $[^2H_6]$dmso. [d] Labelling of *p*-cymene protons:



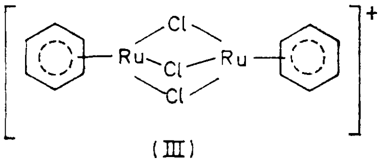
Assignment of resonances to H_A and H_B is arbitrary. Chemical shifts calculated from line positions using formula $(\nu_1 - \nu_3) = (\nu_2 - \nu_4) = [(\delta_A - \delta_B)^2 + J_{AB}^2]^{\frac{1}{2}}$ since an AB rather than AA′BB′ pattern was observed. [e] Peak at τ 4·02 also present due to *ca.* 10% of $[RuCl_2(C_6H_6)]_2$ impurity. [f] J(P–H) < 1·0 Hz. [g] Peak at τ 4·60 also present due to *ca.* 10% of $[RuCl_2(C_6H_6)(PMePh_2)]$ impurity.

ally made by Winkhaus and Singer,[1] though Zelonka and Baird[4] have implied that their sample is more soluble than the original ' polymeric ' complex.

Ligand Reactions.—Pyridine, tertiary phosphines, phosphites, and tertiary arsines (L) cleaved the chlorine bridges of the $[RuCl_2(arene)]_2$ complexes to give orange or red, air-stable complexes $[RuCl_2(arene)L]$ which are monomeric in chloroform (Table 1), in contrast with the original report[1] for $[RuCl_2(C_6H_6)(PBu^n_3)]$. Excess of ligand should be avoided in these preparations otherwise the co-ordinated arene may be displaced, *e.g.* the stoicheiometric quantity of dimethylphenylphosphine with $[RuCl_2(C_6H_6)]_2$ gave $[RuCl_2(C_6H_6)(PMe_2Ph)]$, whereas with an excess of the ligand, the product isolated was $[Ru_2Cl_3(PMe_2Ph)_6]Cl$. As discussed below, some of the tertiary phosphine arene derivatives can also be made by arene exchange from the *p*-cymene complex. The benzene complexes with *N*- or *As*-donor ligands showed a sharp singlet in their proton n.m.r. spectra at τ *ca.* 5 due to co-ordinated benzene, but in the *P*-donor complexes this signal was a closely spaced doublet [J(P–H) 0·5—0·8 Hz] (Table 2). The complexes of the other arenes showed the characteristic upfield shift of the aromatic protons. Neither n.m.r. nor i.r. spectra give any indication of the slight non-planarity found by *X*-ray study of the complexes $[RuCl_2(C_6H_6)(PMePh_2)]$ and $[RuCl_2(p\text{-}MeC_6H_4CHMe_2)(PMePh_2)]$;[5] thus there was no change in the arene signal (apart from slight viscosity broadening) on cooling a solution of $[RuCl_2(C_6H_6)\{P(C_8H_{17})_3\}]$ in $CDCl_3$–CS_2 to −100 °C, and the same is true for solutions of $[RuCl_2(1,3,5\text{-}C_6H_3Me_3)(PBu^n_3)]$ and of $[RuCl_2(C_6Me_6)(PBu^n_3)]$ in CD_2Cl_2–$CHFCl_2$ cooled to −125 °C. Three possible explanations for this behaviour are (*a*) the rings are planar in solution and non-planar in the solid state, (*b*) the rings are non-planar in solution but the proton inequivalence is unresolvably small, or (*c*) the ring is flipping rapidly enough on the n.m.r. time scale that proton equivalence is observed. We are currently examining i.r. and Raman spectra of the complexes $[RuCl_2(C_6H_6)(EMe_3)]$ (E = P or As) in the solid state and in solution to see whether possibility (*a*) can be excluded.

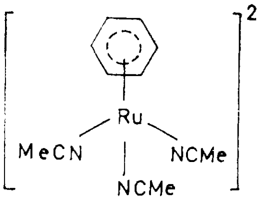
Despite the thermal and oxidative stability of the ruthenium(II) arene complexes, all attempts to prepare them by direct thermal or photochemical reaction of the arenes with ruthenium(II) or ruthenium(III) complexes, *e.g.* $[Ru_2Cl_3(PMePh_2)_6]Cl$, $[RuCl_2(CO)_3]_2$, $[RuCl_2(PPh_3)_3]$, $[RuCl_2(py)_4]$, or $[RuCl_3(PMe_2Ph)_3]$, in the presence or absence of Lewis acids such as $AlCl_3$ or BF_3, or by the reaction of chloride ion with bis(arene) ruthenium(II) complexes, were unsuccessful.

Reaction of the complex $[RuCl_2(C_6H_6)]_2$ with hot water gave an orange solution from which ammonium hexafluorophosphate precipitated an orange solid. The *p*-cymene complex behaved similarly. Analytical data were in agreement with the formula $[Ru_2Cl_3(arene)_2]PF_6$; the benzene complex behaves as a 1 : 1 electrolyte in nitromethane, and the far i.r. spectra of both complexes showed a broad band at *ca.* 260 cm^{-1} (Table 1), suggesting that only bridging chlorine atoms are present. The appearance of a sharp singlet at τ 3·96 in the n.m.r. spectrum of the benzene complex in D_2O shows that η^6-C_6H_6 is still present. We propose the binuclear tri-μ-chloro-bridged structure (III), analogous to that of the cation in $[Ru_2Cl_3(PEt_2Ph)_6]^+[RuCl_3(PEt_2Ph)_3]^-$.[9] An analogous salt, $[Rh_2Cl_3(C_5Me_5)_2]BPh_4$, is formed from the reaction of the complex $[RhCl_2(C_5Me_5)]_2$ with sodium tetraphenylborate.[10] The formation of the complex $[Ru_2Cl_3(arene)_2]^+$ from $[RuCl_2(arene)]_2$ was readily reversed by addition of lithium chloride. Zelonka and Baird[6] have suggested that solutions of the complex $[RuCl_2(C_6H_6)]_2$ in D_2O contain the species $[RuCl(C_6H_6)(D_2O)_2]^+$ and $[Ru(C_6H_6)(D_2O)_3]^{2+}$, to which co-ordinated benzene resonances at τ 4·07 and 3·97 were assigned, but it seems more probable that the latter resonance arises from $[Ru_2Cl_3(C_6H_6)_2]^+$.



(III)

Halide-ion Substitution Reactions.—Reaction of the complex $[RuCl_2(C_6H_6)]_2$ with slightly more than two equivalents of silver(I) tetrafluoroborate in acetonitrile at room temperature gave silver chloride quantitatively. From the solution orange-yellow crystals of the salt $[Ru(C_6H_6)(MeCN)_3](BF_4)_2$ could be isolated, the conductivity of which in nitromethane (Λ_M 223 Ω^{-1} cm^2 mol^{-1}) is consistent with the presence of a 2 : 1 electrolyte (the value is rather high, the quoted range being 150—180 Ω^{-1} cm^2 mol^{-1}, but a number of examples with Λ_M *ca.* 220—230 Ω^{-1} cm^2 mol^{-1} are known[11]). The proton n.m.r. spectrum in CD_3CN showed singlet resonances due to co-ordinated benzene and acetonitrile (Table 2), and the i.r. spectrum showed two ν(CN) bands as expected for a molecule with C_{3v} symmetry (IV) {*cf.* $[Cr(CO)_3(C_6H_6)]$ which shows two ν(CO) bands in solution[12]}. The analogous *p*-cymene complex $[Ru(p\text{-}MeC_6H_4CHMe_2)(MeCN)_3](BF_4)_2$ is an uncrystallisable oil. The dications when treated with chloride ion reformed the complex $[RuCl_2(arene)]_2$.



(IV)

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[9] K. A. Raspin, *J. Chem. Soc.* (*A*), 1969, 461.

[10] J. W. Kang and P. M. Maitlis, *J. Organometallic Chem.*, 1971, **30**, 127.

[11] W. J. Geary, *Co-ordination Chem. Rev.*, 1971, **7**, 81.

[12] R. D. Fischer, *Chem. Ber.*, 1960, **93**, 105.

The reaction of cyclohexa-1,3-diene with ethanolic $RuCl_3$ and an approximately four-fold excess of lithium bromide gave a light brown complex which is not the expected dibromo-complex $[RuBr_2(C_6H_6)]_2$. Its n.m.r. spectrum in [$^2H_6$]dmso showed two peaks due to co-ordinated benzene at τ 3·97 and 4·00 in a ratio of *ca.* 2 : 1. Reaction with tri-n-butylphosphine gave beautiful red needles which also showed two co-ordinated benzene peaks in *ca.* 2 : 1 ratio at τ 4·38 and 4·40; the composition is intermediate between those calculated for $[RuCl_2(C_6H_6)(PBu^n_3)]$ and $[RuBr_2(C_6H_6)(PBu^n_3)]$. The peak at τ 4·38 is readily identified as being due to the complex $[RuBr_2(C_6H_6)(PBu^n_3)]$, and we suggest that the peak at τ 4·40 is due to the bromochloro-species $[Ru(Br)Cl(C_6H_6)(PBu^n_3)]$. This assignment is supported by the observation that addition of the complex $[RuCl_2(C_6H_6)(PBu^n_3)]$ (τ 4·42) to the solution caused a marked decrease in the intensity of the peak at τ 4·38 relative to that at τ 4·40. Repetition of the original reaction with a twenty-fold excess of sodium bromide still gave a mixture of dibromo- and bromochloro-complexes, though the ratio was now *ca.* 3 : 1. A single-crystal *X*-ray examination [13] of the 2 : 1 mixture of tri-n-butylphosphine adducts showed that the compound is homogeneous in the solid state and isomorphous with $[RuCl_2(C_6H_6)(PBu^n_3)]$, so that isomorphous replacement of chloride by bromide ion clearly occurs in this series. Treatment of the complex $[RuCl_2(C_6H_6)(PBu^n_3)]$ with an excess of sodium bromide heated under reflux in butanone gave an inseparable mixture of halogeno-species, whereas under the same conditions, an excess of sodium iodide yielded the pure di-iodo-complex $[RuI_2(C_6H_6)(PBu^n_3)]$. The difference in behaviour between NaBr and NaI is presumably due to the greater solubility of the latter in butanone. Zelonka and Baird [7] report incorrectly that chloride is not substituted by iodide ion in these complexes.

Methylruthenium(II) complexes were prepared in low yield by treatment of $[RuX_2(arene)(PMe_2Ph)]$ ($X = Cl$ or I) with methyl-lithium or methyl Grignard reagents, contrary to Zelonka and Baird's report.[7] The dimethyl complexes $[RuMe_2(arene)(PMe_2Ph)]$ (arene = C_6H_6, *p*-$MeC_6H_4CHMe_2$, or 1,3,5-$C_6H_3Me_3$) were obtained using an excess of methyl-lithium, yields being increased by the addition of 1,4-dioxan to the reaction mixture in order to precipitate lithium halides.[14] The benzene complex is an air-sensitive, yellow, low-melting solid which begins to decompose in the solid state above −40 °C, though its solutions in n-hexane or diethyl ether are appreciably more stable. The complex could only be isolated from the reaction mixture by low-temperature chromatography, and has been characterised by its proton n.m.r. spectrum (Table 2). Both the *p*-cymene and mesitylene complexes are air-sensitive yellow oils, but the mesitylene complex is thermally somewhat more stable than either the benzene or the *p*-cymene complex. It is stable at 0 °C, and decomposes slowly at room temperature in the absence of air. A small quantity of the thermally stable chloro(methyl) complex, $[Ru(Cl)Me(C_6H_6)(PMe_2Ph)]$, was formed in the reaction of $[RuCl_2(C_6H_6)(PMe_2Ph)]$ with methyl-lithium, and was identified by its n.m.r. spectrum (Table 2), which showed two doublets for the inequivalent methyl groups of co-ordinated dimethylphenylphosphine, there being no plane of symmetry through the Ru–P bond. Reaction of the complex $[RuI_2(C_6H_6)(PMe_2Ph)]$ with iodomethylmagnesium gave <10% yield of the analogous orange iodo(methyl) complex. For both the mono- and di-methyl complexes *J*(P–H) for the Ru–Me protons was less than that for the P–Me protons. I.r. spectra of the complexes $[RuMe_2(C_6H_6)(PMe_2Ph)]$ and $[Ru(I)Me(C_6H_6)(PMe_2Ph)]$ showed bands at 1 190 and 1 180 cm^{-1} respectively, which are absent from the spectra of the parent dihalides, and which are tentatively assigned to δ(Me) of the Ru–Me group on the basis of work on methylplatinum(II) complexes.[15] The dimethyl complexes were surprisingly unreactive towards bromine and iodine, only very small amounts of the halogeno(methyl) complexes being formed slowly at room temperature. However, treatment of the complex $[RuMe_2(p\text{-}MeC_6H_4CHMe_2)(PMe_2Ph)]$ with hydrogen chloride in diethyl ether immediately formed the parent dichloride.

The reaction of iodomethylmagnesium in diethyl ether with $[RuCl_2(C_6H_6)L]$ ($L = PBu^n_3$ or PPh_3) in a 1 : 1 ratio gave a *ca.* 4 : 1 ratio of $[RuMe_2(arene)L]$ and $[Ru(I)Me(arene)L]$ as judged by n.m.r. spectra, but the complexes have not been separated or isolated in a pure state. The chloro(methyl) complexes $[Ru(Cl)Me(C_6H_6)L]$ are best prepared by the reaction of $[RuCl_2(C_6H_6)]_2$ in acetonitrile with dimethylmercury or tetramethyltin, and subsequent treatment of the solution with the appropriate tertiary phosphine, as shown by Zelonka and Baird.[7]

Arene-exchange Reactions.—If a solution of an arene complex $[RuCl_2(arene)(PR_3)]$ was heated or irradiated with u.v. light in an aromatic solvent, there was partial or complete exchange of the aromatic groups in addition to general decomposition. The results of our experiments are summarised in Tables **3** and **4**. It is difficult to draw any quantitative conclusions from these data, particularly as it is by no means certain that equilibrium has been reached in some cases, but the following general conclusions seem to be valid.

(*a*) Benzene was displaced only to a small extent from the complex $[RuCl_2(C_6H_6)(PBu^n_3)]$ even by more strongly electron-donating arenes such as toluene, *p*-xylene, hexamethylbenzene, or anisole.

(*b*) Of all the arenes studied *p*-cymene (*p*-$MeC_6H_4CHMe_2$) was the most easily displaced from its PBu^n_3 or PPh_3 complexes. Even cumene, $PhCHMe_2$, completely displaced *p*-cymene from the complex $[RuCl_2(p\text{-}MeC_6H_4CHMe_2)(PBu^n_3)]$ after u.v. irradiation for

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[13] G. B. Robertson, personal communication.

[14] J. Schwartz and J. B. Cannon, *J. Amer. Chem. Soc.*, 1972, **94**, 6226.

[15] D. M. Adams, J. Chatt, and B. L. Shaw, *J. Chem. Soc.*, 1960, 2047.

4 h. Since the *p*-cymene complexes are readily available from α-phellandrene (see above), the displacement method is a useful alternative for the preparation of ruthenium(II) complexes of arenes such as hexamethylbenzene which do not readily undergo metal–ammonia reduction.

(*c*) Arenes having electron-withdrawing substituents such as Cl, F, CF_3, or CO_2Et failed to displace any arene, even *p*-cymene.

TABLE 3

Results of thermally induced arene exchange

Complex	Solvent	Time/h	t/°C	Exchange/%	Recovery (product + starting material)/%
$[RuCl_2(p\text{-}MeC_6H_4CHMe_2)(PBu^n_3)]$	Benzene	6	80	45	52
$[RuCl_2(p\text{-}MeC_6H_4CHMe_2)(PBu^n_3)]$	Benzene	8	70	12	89
$[RuCl_2(p\text{-}MeC_6H_4CHMe_2)(PBu^n_3)]$	Toluene	4	110	100	48
$[RuCl_2(p\text{-}MeC_6H_4CHMe_2)(PBu^n_3)]$	Hexamethylbenzene	5	170	100	21
$[RuCl_2(p\text{-}MeC_6H_4CHMe_2)(PBu^n_3)]$	Hexamethylbenzene [a]	20	100	100	27
$[RuCl_2(p\text{-}MeC_6H_4CHMe_2)(PBu^n_3)]$	Hexamethylbenzene [a]	4	100	44	29
$[RuCl_2(C_6H_6)(PBu^n_3)]$	*p*-Cymene	4	100	0	not measured
$[RuCl_2(C_6H_6)(PBu^n_3)]$	Hexamethylbenzene [a]	4	100	15	29

[a] In n-heptane.

TABLE 4

Results of arene exchange induced by u.v. irradiation (for 4 h at 14 °C unless otherwise stated)

Complex	Solvent	Exchange/%	Recovery (product + starting material)/%
$[RuCl_2(p\text{-}MeC_6H_4CHMe_2)(PBu^n_3)]$	Benzene	57 [a]	35
$[RuCl_2(p\text{-}MeC_6H_4CHMe_2)(PBu^n_3)]$	Toluene	65 [b]	31
$[RuCl_2(p\text{-}MeC_6H_4CHMe_2)(PBu^n_3)]$	Ethylbenzene	*ca.* 50 [c]	18
$[RuCl_2(p\text{-}MeC_6H_4CHMe_2)(PBu^n_3)]$	*o*-Xylene	48	44
$[RuCl_2(p\text{-}MeC_6H_4CHMe_2)(PBu^n_3)]$	*m*-Xylene	52	36
$[RuCl_2(p\text{-}MeC_6H_4CHMe_2)(PBu^n_3)]$	*p*-Xylene	63	51
$[RuCl_2(p\text{-}MeC_6H_4CHMe_2)(PBu^n_3)]$	Mesitylene	25 [d]	51
$[RuCl_2(p\text{-}MeC_6H_4CHMe_2)(PBu^n_3)]$	Cumene	100	13
$[RuCl_2(p\text{-}MeC_6H_4CHMe_2)(PBu^n_3)]$	Anisole	23	29
$[RuCl_2(p\text{-}MeC_6H_4CHMe_2)(PBu^n_3)]$	Ethyl benzoate	0	20
$[RuCl_2(p\text{-}MeC_6H_4CHMe_2)(PBu^n_3)]$	Chlorobenzene	0	35
$[RuCl_2(p\text{-}MeC_6H_4CHMe_2)(PBu^n_3)]$	Trifluorotoluene	0	37
$[RuCl_2(p\text{-}MeC_6H_4CHMe_2)(PPh_3)]$	Benzene	70	46
$[RuCl_2(C_6H_6)(PBu^n_3)]$	*p*-Cymene	0	35
$[RuCl_2(C_6H_6)(PBu^n_3)]$	Toluene	11	40
$[RuCl_2(C_6H_6)(PBu^n_3)]$	*p*-Xylene	11	42
$[RuCl_2(C_6H_6)(PBu^n_3)]$	Cumene	0	50
$[RuCl_2(C_6H_6)(PBu^n_3)]$	Anisole	23	34
$[RuCl_2(C_6H_6)(PBu^n_3)]$	Trifluorotoluene	0	38

[a] 62% After 6 h, 10% recovery. [b] 100% If solution not cooled during irradiation. [c] 5 h Irradiation. [d] 85% After 8 h, 50% recovery.

It would be useful to be able to compare our results with those on arene exchange in Group VI metal tricarbonyl complexes, but unfortunately data are few and occasionally conflicting. Thus, Strohmeier *et al.*[16] state that the rate of exchange of an arene with its $Cr(CO)_3$ complex increases in the order benzene < toluene ≪ cycloheptatriene < naphthalene, but in a later paper[17] referring to the same reaction give the order toluene < benzene < chlorobenzene. Natta *et al.*[18] have carried out exchange reactions analogous to ours by heating a $[Cr(CO)_3(arene)]$ complex with an excess of another arene at *ca.* 170 °C. Although there is no obvious correlation between the nature of the ring substituents and the extent of exchange it is clear that in the $Cr(CO)_3$ series, arenes with electron-withdrawing substituents such as CO_2H, CO_2Me, or CO_2Ph will replace co-ordinated benzene or toluene. This may be a reflection of the greater importance of σ- relative to π-bonding in the ruthenium(II)–arene bond in our complexes compared with that in the chromium(0)–arene bond in $[Cr(CO)_3(arene)]$ complexes. The behaviour of the alkyl-substituted arenes, and particularly the lability of co-ordinated *p*-cymene, can be accounted for qualitatively on the basis of conflicting σ-bonding effects, which should favour co-ordination of alkyl-substituted arenes [*cf.* the increase in metal–ring bond energy in bis(arene)chromium complexes as methyl groups are substituted in the rings[19]], and steric effects, which could disfavour the co-ordination of arenes having bulky substituents. The importance of steric effects in competition with electronic effects in determining which of the two possible staggered conformations is adopted by the $Cr(CO)_3$ complex of an alkyl-substituted

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[16] W. Strohmeier and H. Mittnacht, *Chem. Ber.*, 1960, **93**, 2085.

[17] W. Strohmeier and R. Müller, *Z. phys. Chem.* (*Frankfurt*), 1964, **40**, 85.

[18] G. Natta, R. Ercoli, F. Calderazzo, and F. Santambrogio, *Chimica e Industria*, 1958, **40**, 1003.

[19] E. O. Fischer, S. Schreiner, and A. Reckziegel, *Chem. Ber.*, 1961, **94**, 258; G. E. Herberich and J. Müller, *J. Organometallic Chem.*, 1969, **16**, 111.

arene has already been demonstrated.[20] We note finally that, despite the greater lability of *p*-cymene compared with benzene in our complexes, there is no significant difference in the metal–ring distances observed[5] in the complexes [RuCl$_2$(C$_6$H$_6$)(PMePh$_2$)] and [RuCl$_2$(*p*-MeC$_6$H$_4$CHMe$_2$)(PMePh$_2$)], so that the energy difference between the metal–ring bonds in these complexes is presumably small.

EXPERIMENTAL

All reactions were carried out in a nitrogen atmosphere. U.v. irradiations were carried out with a Pen-ray 5·5 W mercury lamp, model 11SC-1, which fitted into the neck of a 15 cm^3 tube. Melting points were determined on a Gallenkamp m.p. apparatus and are uncorrected. I.r. spectra were measured on PE 225 and 457 spectrophotometers, as Nujol mulls on caesium iodide plates. N.m.r. spectra were measured at 34 °C on Varian HA-100 and Jeolco MH-100 instruments. Conductivities were measured using a Philips GM4144 bridge with a PW9510 conductivity cell. Microanalyses and molecular-weight determinations were carried out in the Analytical Departments of this School and in the John Curtin School of Medical Research. Analytical data, molecular weights, and m.p.s are in Table 1.

Starting Materials.—Cyclohexa-1,3-diene and α-phellandrene were used as received. Cyclohexa-1,4-dienes were prepared by the Birch reduction of arenes.[21] The following modification of the literature method[22] was used to prepare 1,3,5-trimethylcyclohexa-1,4-diene. Lithium (12 g) was added slowly to liquid ammonia (600 cm^3). To the deep blue solution was added dropwise a mixture of mesitylene (50 g) and t-butyl alcohol (110 cm^3) in freshly distilled thf (120 cm^3). The mixture was stirred for 2 h, and methanol (100 cm^3) and water (100 cm^3) were cautiously added. The mixture was set aside overnight. The product was extracted with 3 × 200 cm^3 portions of diethyl ether, dried (Na$_2$SO$_4$), and distilled to yield 21 g (41%) of the required diene, b.p. 148—150 °C/712 mm.

Preparation of [RuX$_2$(arene)]$_2$ *Complexes.*—*Di-μ-chloro-bis*[(*η-benzene*)*chlororuthenium*(II)]. Hydrated ruthenium(III) trichloride (2·0 g) in ethanol 100 cm^3) was heated under reflux with cyclohexadiene (either 1,3- or 1,4-) (10 cm^3) for 4 h. The brown precipitate was filtered off, washed with methanol, and dried *in vacuo* (1·83 g, 95%). The analogous *bromo-complex* was prepared similarly from hydrated ruthenium(III) tribromide. Yield: 1·3 g (53%). Similarly prepared were the complex [RuCl$_2$(*p*-cymene)]$_2$ from α-phellandrene (4 h, 65%), [RuCl$_2$(mesitylene)]$_2$ from 1,3,5-trimethylcyclohexa-1,4-diene (16 h, 90%), and [RuCl$_2$(anisole)]$_2$ from 1-methoxycyclohexa-1,4-diene (30 h, 25%) in methanol (100 cm^3).

Di-μ-chloro-bis[*chloro*(*η*-p-*xylene*)*ruthenium*(II)]. Hydrated ruthenium(III) trichloride (1·5 g) in ethanol (65 cm^3) was heated under reflux with 1,4-dimethylcyclohexa-1,4-diene (3 cm^3). After 3 h the black solid which had precipitated was centrifuged. The supernatant orange-brown solution was stirred at room temperature for 2 days. The dark orange precipitate which formed was filtered off, washed with methanol, and dried *in vacuo* (0·1 g, 6%).

Di-μ-iodo-bis[(*η-benzene*)*iodoruthenium*(II)].— Hydrated ruthenium(III) trichloride (1·0 g) in ethanol (50 cm^3) was stirred with sodium iodide (11·5 g, twenty-fold excess) for 6 h. Cyclohexa-1,3-diene (5 cm^3) was added and the mixture heated under reflux for 18 h. The dark red precipitate was filtered, washed thoroughly with water and methanol, and dried *in vacuo* (1·40 g, 84%).

Cleavage of Co-ordinated Arene from [RuCl$_2$(anisole)]$_2$.—A solution of sodium cyanide (0·25 g) in water (6 cm^3) was treated with solid [RuCl$_2$(anisole)]$_2$ (0·05 g) and the mixture heated under reflux for 1 h. The solution was extracted with CCl$_4$ (2 × 5 cm^3) and dried (MgSO$_4$). Its i.r. spectrum was identical with that of an authentic sample of anisole in CCl$_4$.

Preparation of [RuCl$_2$(arene)L]*Complexes.*—*η-Benzenedichloro*(*tri-n-butylphosphine*)*ruthenium*(II). The complex [RuCl$_2$(C$_6$H$_6$)]$_2$ (0·5 g) suspended in benzene (20 cm^3) was heated under reflux with an excess of tri-n-butylphosphine (1 ml) for 4 h. Solvent was removed under reduced pressure, and the residual brown solid was recrystallised from dichloromethane–hexane to give red crystals of the *complex* (0·55 g, 60%). Similarly prepared from [RuCl$_2$(C$_6$H$_6$)]$_2$ and the appropriate ligand were the *dichloro-complexes* of tri-n-octylphosphine (brown solid, 80%), dimethylphenylphosphine (red crystals, 66%), methyldiphenylphosphine (red crystals, 70%), triphenylphosphine (red crystals, 60%, from chloroform–n-heptane), trimethylarsine (red crystals, 27%), and dimethylphenylarsine (red crystals, 33%, from chloroform–n-heptane), and from [RuBr$_2$(C$_6$H$_6$)]$_2$ and the appropriate ligand the *dibromo-complexes* of tri-n-butylphosphine (dark red crystals, 64%) and methyldiphenylphosphine (dark red crystals, 65%).

η-Benzenedichloro(*trimethyl phosphite*)*ruthenium*(II). The complex [RuCl$_2$(C$_6$H$_6$)]$_2$ (0·1 g) suspended in benzene (15 cm^3) was heated to 70 °C with an equimolar amount of trimethyl phosphite (0·05 g) for 1 h. The brown solution was evaporated to dryness, and the residue was washed with n-pentane (3 × 5 cm^3). The brown solid was dissolved in chloroform (10 cm^3), the solution filtered, and evaporated to dryness under reduced pressure. The resulting red-brown *complex* was dried *in vacuo* (0·06 g, 40%).

η-p-*Cymenedichloro*(*tri-n-butylphosphine*)*ruthenium*(II). The complex [RuCl$_2$(*p*-cymene)]$_2$ (0·37 g) suspended in n-hexane (20 cm^3) was heated under reflux with tri-n-butylphosphine (0·4 g) for 4 h. Supernatant liquid was decanted and the red solid was recrystallised from dichloromethane–hexane. The red crystals of the *complex* were dried *in vacuo* (0·52 g, 85%). Similarly prepared from [RuCl$_2$(*p*-cymene)]$_2$ and the appropriate ligand were the *dichloro-complexes* of methyldiphenylphosphine (red crystals, 75%), triphenylphosphine (red crystals, 90%), and pyridine (orange crystals, 77%).

η-p-*Cymenedichloro*(*dimethylphenylphosphine*)*ruthenium*(II). The complex [RuCl$_2$(*p*-cymene)]$_2$ (0·2 g) was heated to 40 °C with an excess of dimethylphenylphosphine (3 cm^3) for 4 h. The red product was extracted with dichloromethane (20 cm^3), and the solution was filtered. On evaporation to *ca.* 5 cm^3, red crystals were formed. The mother liquor was decanted, and the crystals were recrystallised from dichloromethane–light petroleum (b.p. 40—60 °C) and dried *in vacuo* (0·18 g, 60%). The analogous *dimethylphenylarsine complex* was prepared similarly as orange-red crystals (36% yield).

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The following complexes were prepared as for $[\mathrm{RuCl_2}(p\text{-cymene})(\mathrm{PBu^n_3})]$: *dichloro(methyldiphenylphosphine)(η-p-xylene)ruthenium*(II) (red solid, 85%); *η-anisoledichloro(methyldiphenylphosphine)ruthenium*(II) (red crystals, 68%); *dichloro(η-toluene)(tri-n-butylphosphine)ruthenium*(II) (red crystals, 65%); and *dichloro(dimethylphenylphosphine)(η-mesitylene)ruthenium*(II) (red crystals, 75%).

Dichloro(η-mesitylene)(pyridine)ruthenium(II). The complex $[\mathrm{RuCl_2(mesitylene)}]_2$ (0·3 g) was heated under reflux with pyridine (15 cm³) for 2 h. Hexane (20 cm³) was added, and the red solid which precipitated was filtered off. Recrystallisation from dichloromethane–hexane gave orange-red crystals of the *complex* (0·3 g, 78%).

η-Benzene(dimethylphenylphosphine)di-iodoruthenium(II). The complex $[\mathrm{RuI_2(C_6H_6)}]_2$ (1·5 g) in benzene (50 cm³) was heated under reflux with dimethylphenylphosphine (0·5 g) for 12 h. Chloroform (50 cm³) was added and the solution was filtered. Evaporation under reduced pressure and cooling gave deep red crystals of the *complex* (1·90 g, 95%).

Cationic Complexes.—Tri-μ-chloro-bis[benzeneruthenium-(II)] *hexafluorophosphate*, $[\mathrm{Ru_2Cl_3(C_6H_6)_2}]\mathrm{PF_6}$. The complex $[\mathrm{RuCl_2(C_6H_6)}]_2$ (0·2 g) was heated under reflux with water (10 cm³) for 2 h. The orange solution was filtered and treated with a saturated aqueous solution of ammonium hexafluorophosphate. After 3 days, the orange *precipitate* was filtered off, washed with water and methanol, and dried *in vacuo* (0·1 g, 41%). The *p-cymene complex* was prepared similarly from $[\mathrm{RuCl_2}(p\text{-cymene})]_2$ (0·2 g) and was recrystallised from chloroform to give orange crystals (0·16 g, 68%).

Reaction of $[\mathrm{Ru_2Cl_3(C_6H_6)_2}]\mathrm{PF_6}$ *with* LiCl. A mixture of the complex $[\mathrm{Ru_2Cl_3(C_6H_6)_2}]\mathrm{PF_6}$ (0·1 g), and lithium chloride (0·1 g, in excess) was heated under reflux in ethanol (10 cm³). After 16 h, a red-brown precipitate had formed. Ethanol was removed under reduced pressure, and the residual solid washed with acetone and dried *in vacuo*. It was identified from its i.r. spectrum as $[\mathrm{RuCl_2(C_6H_6)}]_2$ (0·07 g, 85%).

Tris(acetonitrile)(η-benzene)ruthenium(II) *bis(tetrafluoroborate)*, $[\mathrm{Ru(C_6H_6)(MeCN)_3}](\mathrm{BF_4})_2$. The complex $[\mathrm{RuCl_2(C_6H_6)}]_2$ (0·5 g) in acetonitrile (15 cm³) was treated with silver(I) tetrafluoroborate (0·9 g, 2·3 equiv.) and stirred at 35 °C for 2 h. Silver(I) chloride (0·55 g; calc. for 2 equivs., 0·57 g) was filtered off to give a clear yellow solution. After 2 days at 0 °C, yellow-orange crystals of the *complex* had formed (0·36 g, 38%). The *p-cymene complex* was prepared similarly from $[\mathrm{RuCl_2}(p\text{-cymene})]_2$ to give a yellow oil (45% yield) which could not be crystallised.

Halide-exchange Reactions.—(*a*) A mixture of hydrated ruthenium(III) trichloride (0·71 g), lithium bromide (0·91 g, *ca.* four-fold excess) and cyclohexa-1,3-diene (5 cm³) in ethanol (30 cm³) was set aside for 1 month. The red-brown precipitate of the mixed *bromochloro-complex* was centrifuged off, washed with methanol, and dried *in vacuo* (0·77 g) (Found: C, 24·1; H, 2·3. Calc. for $\mathrm{C_6H_6Br_2Ru}$: C, 21·3; H, 1·8. Calc. for $\mathrm{C_6H_6Cl_2Ru}$: C, 28·8; H, 2·4%). N.m.r. spectrum ([²H₆]dmso): τ 3·98 (s) and 4·00 (s) (*ca.* 2 : 1 ratio, $\mathrm{C_6}H_6$).

The bromochloro-complex (0·43 g) and tri-n-butylphosphine (3 cm³) were heated at 120 °C for 3 h. After cooling to room temperature, the mixture was extracted with dichloromethane–light petroleum (b.p. 40—60 °C) (1 : 3, 2 × 10 cm³) to remove the excess of tri-n-butylphosphine, and the residue was then extracted with hot dichloromethane–n-heptane (3 : 1, 3 × 20 cm³). The solution was filtered and evaporated under reduced pressure until solid began to form. It was then set aside at room temperature for several days; beautiful red needles of the tri-n-butylphosphine *adduct* separated (0·3 g) (Found: C, 41·6; H, 6·4. Calc. for $\mathrm{C_{18}H_{33}Br_{1\cdot67}Cl_{0\cdot33}Ru}$: C, 41·0; H, 6·3%). N.m.r. spectrum ($\mathrm{CDCl_3}$): τ 4·38 [d, *J*(P–H) 0·8 Hz, $[\mathrm{RuBr_2(C_6}H_6)]$}, 4·40 {d, *J*(P–H) 0·8 Hz, $[\mathrm{Ru(Cl)Br(C_6}H_6)]$} (*ca.* 2 : 1 ratio), 7·9 (m), 8·5 (m), and 9·0 (m) (n-butyl protons). Repetition of the experiment (*a*) using a twenty-fold excess of sodium bromide, and heating the mixture under reflux for 4 h, gave a brown solid which showed peaks in its n.m.r. spectrum at τ 3·98 and 4·00 in a ratio of *ca.* 3 : 1.

(*b*) *Reaction of* $[\mathrm{RuCl_2}(p\text{-cymene})(\mathrm{PBu^n_3})]$ *with* NaBr. The complex $[\mathrm{RuCl_2}(p\text{-cymene})(\mathrm{PBu^n_3})]$ (0·03 g) and sodium bromide (0·19 g) were heated under reflux in butan-2-one (10 cm³) for 17 h. The solution was evaporated to dryness under reduced pressure; the solid was washed with water, extracted with dichloromethane, and dried ($\mathrm{MgSO_4}$). The red solution was filtered, evaporated to small volume, and the *product* precipitated by addition of n-hexane. Its i.r. spectrum showed the presence of a number of bands in the ν(RuCl) region, and a new band at 205 cm⁻¹ due to ν(RuBr), and its n.m.r. spectrum showed a broad singlet at τ 4·62 (*cf.* starting material, τ 4·58). Clearly a mixture of products was present.

(*c*) *Reaction of* $[\mathrm{RuCl_2(C_6H_6)(PBu^n_3)}]$ *with* NaI. The complex $[\mathrm{RuCl_2(C_6H_6)(PBu^n_3)}]$ (0·1 g) in butan-2-one (20 cm³) was heated under reflux with sodium iodide (1·3 g) for 1 h. The solution was evaporated to dryness, and the brown solid was washed with water. The residue was extracted with dichloromethane, the solution dried ($\mathrm{MgSO_4}$), and then evaporated under reduced pressure until solid began to precipitate. Addition of light petroleum (b.p. 40—60 °C) gave dark red crystals of impure *benzene-di-iodo(tri-n-butylphosphine)ruthenium*(II) (0·11 g), which showed only one peak due to co-ordinated benzene at τ 4·28. Chromatography on alumina and elution with chloroform separated the complex from a yellow, unidentified impurity. The product was finally recrystallised from $\mathrm{CHCl_3}$–MeOH.

σ-Methyl Derivatives.—Reaction of $[\mathrm{RuCl_2(C_6H_6)(PMe_2Ph)}]$ *with* MeLi. A suspension of the complex $[\mathrm{RuCl_2(C_6H_6)(PMe_2Ph)}]$ (0·8 g) in diethyl ether (10 cm³) was cooled to −50 °C and treated dropwise with methyl-lithium in diethyl ether (5 equivs.). The mixture was stirred and allowed to warm to −30 °C. After 2 h, 1,4-dioxan (1 cm³) was added and stirring continued for a further 2 h. The reaction mixture was then filtered under an atmosphere of nitrogen and chromatographed at −50 °C on neutral alumina which had been freshly deaerated and de-activated. Elution with diethyl ether gave a yellow solution which, on evaporation to small volume and cooling to −78 °C, gave a yellow solid; this darkened on warming to room temperature. It was identified as *η-benzenedimethyl(dimethylphenylphosphine)ruthenium*(II), $[\mathrm{RuMe_2(C_6H_6)(PMe_2Ph)}]$, from its proton n.m.r. spectrum (Table 1). Purification and elemental analysis were impossible owing to the thermal instability of the complex.

In a second experiment, after addition of 1,4-dioxan and stirring at −30 °C for 2 h, diethyl ether was removed under reduced pressure. The residue was extracted with benzene (2 × 5 cm³), and the extract chromatographed on neutral alumina. Diethyl ether eluted two bands, the first of which contained the complex $[RuMe_2(C_6H_6)(PMe_2Ph)]$ (n.m.r. identification). The second band gave a yellow solid which was identified from its n.m.r. spectrum (Table 1) as *η-benzenechloro(dimethylphenylphosphine)(methy)ruthenium*(II), $[Ru(Cl)Me(C_6H_6)(PMe_2Ph]$ ($<10\%$-yield).

Reaction of $[RuI_2(C_6H_6)(PMe_2Ph)]$ *with* MeMgI. A suspension of $[RuI_2(C_6H_6)(PMe_2Ph)]$ (0·8 g) in diethyl ether (15 cm^3) was cooled to −40 °C and treated dropwise with iodomethylmagnesium (1·5 equiv.) in diethyl ether for 3 h with stirring. The orange solution was filtered under an atmosphere of nitrogen to remove unreacted $[RuI_2(C_6H_6)(PMe_2Ph)]$, and was chromatographed on deaerated, deactivated neutral alumina at 0 °C. Diethyl ether eluted an orange band which, on evaporation and cooling to −78 °C, gave an orange solid, *η-benzene(dimethylphenyl phosphine)iodo(methyl)ruthenium*(II), $[Ru(I)Me(C_6H_6)(PMe_2Ph)]$, in $<10\%$ yield.

(Dimethylphenylphosphine)(η-mesitylene)dimethylruthenium (II), $[RuMe_2(1,3,5\text{-}C_6H_3Me_3)(PMe_2Ph)]$. A suspension of the complex $[RuCl_2(\text{mesitylene})(PMe_2Ph)]$ (0·5 g) in diethyl ether (10 cm^3) was stirred at 0 °C with methyl-lithium (15 cm^3 of a 5% solution) in ether for 2 h in a nitrogen atmosphere. Methanol was added to destroy the excess of methyl-lithium and the solution was evaporated to dryness under reduced pressure. The residue was extracted with n-pentane. The solution was filtered and on evaporation gave a yellow *oil*, which was dried *in vacuo* at 0 °C. The complex was stable at this temperature, but decomposed slowly at room temperature. Exposure to air caused rapid decomposition.

Reaction of $[RuCl_2(C_6H_6)(PPh_3)]$ *with methyl-lithium.* The complex $[RuCl_2(C_6H_6)(PPh_3)]$ (0·2 g) in diethyl ether (10 cm^3) was stirred under an atmosphere of nitrogen with methyl-lithium (2 cm^3 of a 5% solution in ether, excess) at −78 °C and allowed to warm to room temperature over a 2 h period. Diethyl ether was evaporated from the green solution, and the product extracted with benzene. Benzene was removed *in vacuo* to leave a brown oil, the n.m.r. spectrum of which (Table 2) showed the presence of a mixture of the complexes $[RuMe_2(C_6H_6)(PPh_3)]$ (main product) and $[Ru(Cl)Me(C_6H_6)(PPh_3)]$. Attempts to purify these complexes by chromatography were not successful.

Arene-exchange Reactions.—Typical examples are described. Results are summarised in Tables 3 and 4.

The complex $[RuCl_2(p\text{-cymene})(PBu^n{}_3)]$ (0·04 g) in benzene (10 cm^3) was irradiated in a water-cooled vessel for 4 h under a nitrogen atmosphere. The resulting brown solution was evaporated to dryness under reduced pressure and the residue, dissolved in chloroform, was chromatographed on neutral alumina. The single red band was collected, and the solution was evaporated to dryness to yield a red solid, the composition of which was determined from its proton n.m.r. spectrum (Table 2).

The complex $[RuCl_2(p\text{-cymene})(PBu^n{}_3)]$ (0·05 g) in toluene (20 cm^3) was heated under reflux for 4 h. The solution was then worked up as above to yield a red solid (0·022 g, 48%) which was analysed on the basis of its n.m.r. spectrum (Table 2).

The complex $[RuCl_2(p\text{-}MeC_6H_4CHMe_2)(PBu^n{}_3)]$ (0·25 g) was stirred under an atmosphere of nitrogen with hexamethylbenzene (10 g) at 170 °C for 5 h. The mixture was cooled and hexamethylbenzene removed by repeated washing with hexane followed by chromatography on neutral alumina. Elution with chloroform gave a single red band from which red crystals of *dichloro(η-hexamethylbenzene)(tri-n-butylphosphine)ruthenium*(II) were obtained by evaporation and recrystallisation from chloroform–n-heptane (0·14 g, 21%).

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