Reactions of (η^6-arene)(η^6-[2.2]paracyclophane)ruthenium(II) Complexes with Nucleophiles

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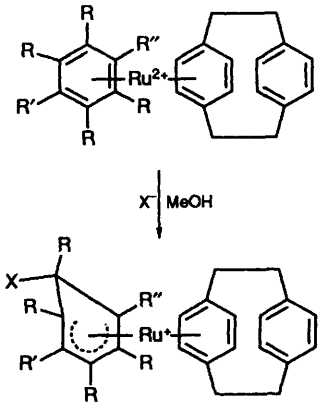
Single addition of the nucleophiles $X^- = H^-$, CN^- or OH^- to (η^6-arene)(η^6-[2.2]paracyclophane)-ruthenium(II) tetrafluoroborate (arene = benzene, *p*-cymene, 1,4-diisopropylbenzene or hexamethylbenzene) and the osmium(II) η^6-C_6H_6 analogue produces the (η^5-cyclohexadienyl)(η^6-[2.2]paracyclophane)metal(II) complexes as the sole products. These compounds have been identified by ^{1}H NMR and by infrared spectroscopy. The expected isotope shift is observed when $Na[BD_4]$ is used in place of $Na[BH_4]$. The steric factors influencing the site of nucleophilic attack are discussed and nucleophilic addition to $[Ru(\eta^6\text{-}C_{16}H_{16})_2][BF_4]_2$ is also examined.

Both single and double nucleophilic addition to co-ordinated arenes is of significant interest as a synthetic route to arene functionalisation[1] and a single nucleophilic attack is a key initial step in the recently reported synthesis of (±)-dihydroxyserrulatic acid.[2] While bis(arene)ruthenium complexes are expected[3] to be around thirty times less electrophilic than their iron analogues they display a number of advantages which make them the more attractive alternative in this type of work. These advantages include (*a*) the ready availability, *via* the Bennett[4] and Rybinskaya[5,6] syntheses, of unsymmetrical complexes and (*b*) the elimination of interfering electron-transfer reactions[7–9] which can occur on the addition of carbon-donor nucleophiles and result in the formation and often rapid decomposition of unstable nineteen- and twenty-electron species. Use of the highly sterically hindered [2.2]paracyclophane ligand has recently been shown to direct nucleophilic attack onto less-hindered arenes co-ordinated to the same metal centre[10] to produce η^4-diene complexes such as $[Ru(\eta^6\text{-}C_{16}H_{16})(\eta^4\text{-}C_6Me_6H_2)]$ ($C_6Me_6H_2$ = 1,2,3,4,5,6-hexamethylcyclohexa-1,4-diene). In addition, protonation of an η^4-[2.2]paracyclophane compound gives a co-ordinated η^5-cyclophane with the added hydrogen atom in the *endo* position.[10] That reaction is believed to involve the initial formation of a metal hydride followed by proton transfer to the carbocyclic ring. We now report the use of the [2.2]paracyclophane ligand to direct *single* nucleophilic attack onto a number of η^6-arenes and examine the question of *exo* or *endo* addition by a study of the effects of deuterium isotopic substitution on solid-state infrared and solution ^{1}H NMR spectra.

A preliminary report of part of this work has been published.[11]

Results and Discussion

Treatment of an almost colourless methanolic suspension of $[Ru(\eta^6\text{-}C_{16}H_{16})(\eta^6\text{-}C_6H_6)][BF_4]_2$ **1** with $Na[BH_4]$ gives a rapid darkening to deep green, possibly indicative of the formation of an intermediate charge-transfer complex.[7,9] Extraction of the reaction mixture with dichloromethane and precipitation gives the stable bright yellow cyclohexadienyl complex $[Ru(\eta^6\text{-}C_{16}H_{16})(\eta^5\text{-}C_6H_7)][BF_4]$ **2** in *ca.* 40% yield as the sole product (Scheme 1). A similar synthetic procedure utilising KCN gives the mildly air-sensitive complex $[Ru(\eta^6\text{-}C_{16}H_{16})(\eta^5\text{-}C_6H_6CN)][BF_4]$ **3**. Proton NMR data for these complexes are summarised in Table 1. The singlet resonance for the benzene ligand in the parent compound is replaced with one multiplet and three triplet resonances covering a wide chemical shift range (*e.g.* δ 6.20, 4.86, 3.33 and 2.32 for compound **2**)



Scheme 1 Nucleophilic addition to (arene)([2.2]paracyclophane)-ruthenium(II) dications. R = H or Me; R′, R″ = H, Me or Pr^i; X = H, CN or OH

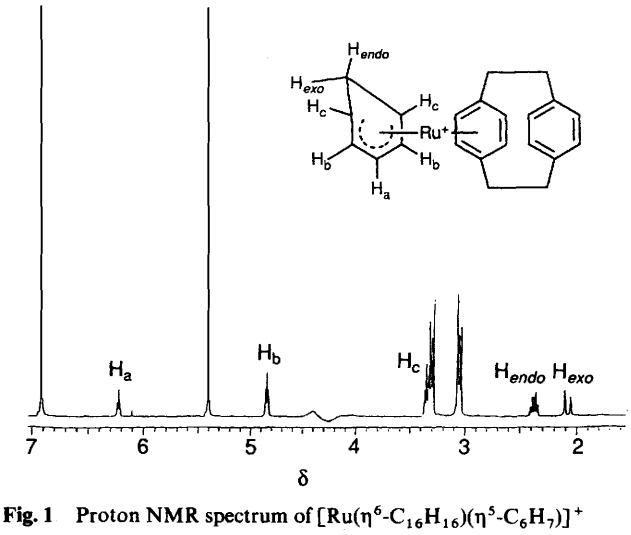


Fig. 1 Proton NMR spectrum of $[Ru(\eta^6\text{-}C_{16}H_{16})(\eta^5\text{-}C_6H_7)]^+$

consistent with previous observations[12] and indicative of the formation of a cyclohexadienyl complex. In addition a widely spaced doublet resonance ($^2J_{HH}$ = 13.5 Hz) is observed at δ 2.06 and is assigned to H_{exo} (Fig. 1). Vicinal coupling to H_c is not observed since the dihedral angle between the two protons H_c and H_{exo} is close to 90°. In the infrared spectrum **2** exhibits

Table 1 Proton NMR data for new compounds[a]

Compound	δ, J_{HH}/Hz		
	Cyclophane		
	Aromatic decks	Bridge	Cyclohexadienyl
2 $[Ru(\eta^6\text{-}C_{16}H_{16})(\eta^5\text{-}C_6H_7)][BF_4]$	6.84 (s, 4, H), 5.36 (s, 4 H)	3.26, 3.02 (AA'XX', 8 H)	6.20 (t, 1 H, ^3J = 5.1), 4.86 (t, 2 H, ^3J = 5.6), 3.33 (t, 2 H, ^3J = 6.6), 2.32 (m, 1 H), 2.06 (d, 1 H, ^2J = 13.5)
2′ $[Ru(\eta^6\text{-}C_{16}H_{16})(\eta^5\text{-}C_6H_6D)][BF_4]$	6.84 (s, 4 H), 5.31 (s, 4 H)	3.29, 3.00 (AA'XX', 8 H)	6.21 (t, 1 H, ^3J = 5.2), 4.87 (t, 2 H, ^3J = 5.5), 3.35 (t, 2 H[b]), 2.29 (t, 1 H, ^3J = 5.4)
3 $[Ru(\eta^6\text{-}C_{16}H_{16})(\eta^5\text{-}C_6H_6CN)][BF_4]$[c]	6.84 (s, 4 H), 5.42 (s, 4 H)	3.23, 2.92 (AA'XX', 8 H)	6.30 (t, 1 H, ^3J = 4.9), 4.94 (t, 2 H, ^3J = 5.7), 3.47 (t, 2 H, ^3J = 6.3), 3.43 (q, 1 H, ^3J = 6.0)
4 $[Os(\eta^6\text{-}C_{16}H_{16})(\eta^5\text{-}C_6H_7)][BF_4]$	6.95 (s, 4 H), 5.57 (s, 4 H)	3.34, 2.97 (AA'XX', 8 H)	6.58 (t, 1 H, ^3J = 5.1), 5.19 (t, 2 H, ^3J = 5.4), 3.63 (t, 2 H, ^3J = 5.9), 3.58 (d, 1 H, ^2J = 12.4), 2.33 (m, 1 H)
6a $[Ru(\eta^6\text{-}C_{16}H_{16})(\eta^5\text{-}4\text{-}MeC_6H_5CHMe_2)][BF_4]$ Minor isomer	6.83 (s, 4 H), 5.54, 5.04 (AB, 4 H, ^3J = 6.7)	3.23 (m, 4 H), 2.94 (m, 2 H), 2.82 (m, 2 H)	6.05 (d, 1 H, ^3J = 4.6), 4.70 (d, 1 H[b]), 3.44 (d, 1 H[b]), 2.32 (dd, 1 H[b]), 2.08 (d, 1 H, ^2J = 13.2), 1.71 (s, 3 H), 1.65 (spt, 1 H, ^3J = 6.7), 0.90 (d, 3 H, ^3J = 6.8), 0.78 (d, 3 H, ^3J = 6.9)
6b $[Ru(\eta^6\text{-}C_{16}H_{16})(\eta^5\text{-}4\text{-}MeC_6H_5CHMe_2)][BF_4]$ Major isomer	6.84 (s, 4 H), 5.61, 5.02 (AB, 4 H, ^3J = 6.1)	3.23 (m, 4 H), 2.94 (m, 2 H), 2.82 (m, 2 H)	5.95 (d, 1 H, ^3J = 4.4), 4.71 (d, 1 H, ^3J = 4.8), 3.44 (d, 1 H, ^3J = 6.2), 2.34 (dd, 1 H, ^3J = 6.2, ^2J = 13.2), 2.24 (d, 1 H, ^2J = 13.2), 1.36 (s, 3 H), 1.88 (spt, 1 H, ^3J = 6.8), 0.97 (d, 3 H, ^3J = 7.1), 0.95 (d, 3 H, ^3J = 7.7)
$[Ru(\eta^6\text{-}C_{16}H_{16})(\eta^5\text{-}4\text{-}MeC_6H_5CHMe_2)][BPh_4]$[d] Minor isomer	6.67, 6.63 (AB, 4 H, ^3J = 7.1), 4.86, 4.28 (AB, 4 H, ^3J = 6.0)	3.13 (m, 4 H), 2.68 (m, 2 H), 2.55 (m, 2 H)	5.58 (d, 1 H, ^3J = 5.0), 4.28 (d, 1H[d]), 3.19 (br s, 1 H), 2.17 (m, 1 H), 2.02 (d, 1 H, ^2J = 13.1), 1.52 (s, 3 H), 1.46 (spt, 1 H, ^3J = 5.3), 0.85 (d, 3 H, ^3J = 7.0), 0.74 (d, 3 H, ^3J = 6.9)
$[Ru(\eta^6\text{-}C_{16}H_{16})(\eta^5\text{-}4\text{-}MeC_6H_5CHMe_2)][BPh_4]$[d] Major isomer	6.67, 6.63, (AB, 4 H, ^3J = 7.1), 4.90, 4.25 (AB, 4 H, ^3J = 5.7)	3.13 (m, 4 H), 2.68 (m, 2 H), 2.55 (m, 2 H)	5.64 (d, 1 H, ^3J = 5.4), 4.20 (d, 1 H, ^3J = 5.3), 3.19 (br s, 1 H), 2.17 (m, 1 H), 2.17 (d, 1 H, ^2J = 12.4), 1.71 (spt, 1 H, ^3J = 6.8), 1.19 (s, 3 H), 0.92 (dd, 3 H, ^3J = 3.7), 0.86 (m, 3 H)
6a′ $[Ru(\eta^6\text{-}C_{16}H_{16})(\eta^5\text{-}4\text{-}MeC_6H_4DCHMe_2)][BF_4]$ Minor isomer	6.87 (s, 4 H), 5.63, 5.09 (AB, 4 H, ^3J = 5.8)	3.28 (m, 4 H), 2.90 (m, 2 H), 2.86 (m, 2 H)	6.13 (d, 1 H, ^3J = 5.0), 4.77 (d, 1 H, ^3J = 4.7), 3.36 (d, 1 H, ^3J = 6.7), 2.30 (d, 1 H, ^3J = 6.0), 1.76 (s, 3 H), 1.66 (spt, 1 H, ^3J = 6.5), 0.93 (d, 3 H, ^3J = 7.0), 0.81 (d, 3 H, ^3J = 6.9)
6b′ $[Ru(\eta^6\text{-}C_{16}H_{16})(\eta^5\text{-}4\text{-}MeC_6H_4DCHMe_2)][BF_4]$ Major isomer	6.88 (s, 4 H), 5.70, 5.09 (AB, 4 H, ^3J = 5.8)	3.28 (m, 4 H), 2.90 (m, 2 H), 2.86 (m, 2 H),	6.01 (d, 1 H, ^3J = 4.7), 4.83 (d, 1 H, ^3J = 4.4), 3.36 (d, 1 H, ^3J = 8.9), 2.34 (d, 1 H, ^3J = 6.0), 1.91 (spt, 1 H, ^3J = 6.7), 1.41 (s, 3 H), 1.01 (d, 3 H, ^3J = 6.7), 0.98 (d, 3 H, ^3J = 6.6)
7a $[Ru(\eta^6\text{-}C_{16}H_{16})\{\eta^5\text{-}4\text{-}MeC_6H_4CHMe_2\text{-}(CN)\}][BF_4]$ Minor isomer	6.86 (s, 4 H), 5.82, 5.22 (AB, 4H[d])	3.26 (m, 4 H), 2.98 (m, 2 H), 2.84 (m, 2 H)	6.28 (d, 1 H, ^3J = 5.6), 5.01 (d, 1 H, ^3J = 5.4), 3.74 (d, 1 H[d]), 3.48 (d, 1 H, ^3J = 6.0), 1.85 (s, 3 H), 1.80 (m, 1 H), 1.01 (m, 6 H)
7b $[Ru(\eta^6\text{-}C_{16}H_{16})\{\eta^5\text{-}4\text{-}MeC_6H_4CHMe_2\text{-}(CN)\}][BF_4]$ Major isomer	6.86 (s, 4 H), 5.83, 5.22 (AB, 4 H, ^3J = 6.4)	3.26 (m, 4 H), 2.98 (m, 2 H), 2.84 (m, 2 H)	6.13 (d, 1 H, ^3J = 5.5), 4.91 (d, 1 H, ^3J = 5.4), 3.70 (d, 1 H, ^3J = 6.2), 3.54 (d, 1 H, ^3J = 6.2), 2.01 (spt, 1 H, ^3J = 6.8), 1.52 (s, 3 H), 1.05 (d, 3 H, ^3J = 6.9), 1.04 (d, 3 H, ^3J = 6.9)
8 $[Ru(\eta^6\text{-}C_{16}H_{16})\{\eta^5\text{-}1,4\text{-}(Me_2CH)_2C_6H_5\}][BF_4]$	6.82 (s, 4 H), 5.59, 5.04 (AB, 4 H, ^3J = 6.3)	3.24 (m, 4 H), 2.96 (m, 2 H), 2.82 (m, 2 H)	6.05 (d, 1 H, ^3J = 5.1), 4.78 (d, 1 H, ^3J = 5.1), 3.38 (d, 1 H, ^3J = 6.5), 2.36 (dd, 1 H, ^3J = 6.5, ^2J = 13.4), 2.10 (d, 1 H, ^2J = 13.4), 1.92 (spt, 1 H, ^3J = 6.7), 1.68 (spt, 1 H, ^3J = 6.7), 1.04 (d, 3 H, ^3J = 6.8), 0.94 (d, 3 H, ^3J = 6.7), 0.92 (d, 3 H, ^3J = 6.7), 0.80 (d, 3 H, ^3J = 6.7)
10 $[Ru(\eta^6\text{-}C_{16}H_{16})(\eta^5\text{-}C_6Me_6H)][BF_4]$	6.81 (s, 4 H), 5.04 (s, 4 H)	3.23, 2.86 (AA'XX', 8 H)	2.28 (s, 3 H), 2.00 (q, 1 H, ^3J = 6.7), 1.87 (s, 6 H), 1.34 (s, 6 H), 1.01 (d, 3 H, ^3J = 7.0)
10′ $[Ru(\eta^6\text{-}C_{16}H_{16})(\eta^5\text{-}C_6Me_6D)][BF_4]$	6.83 (s, 4 H), 5.10 (s, 4 H)	3.26, 2.88 (AA'XX', 8 H)	2.30 (s, 3 H), 1.89 (s, 6 H), 1.36 (s, 6 H), 1.02 (s, 3 H)
11 $[Ru(\eta^6\text{-}C_{16}H_{16})(\eta^5\text{-}C_6Me_6CN)][BF_4]$	6.87 (s, 4 H), 5.30 (s, 4 H)	3.30, 2.90 (AA'XX', 8 H)	2.37 (s, 3 H), 2.01 (s, 6 H), 1.50 (s, 6 H), 1.46 (s, 3 H)
12 $[Ru(\eta^6\text{-}C_{16}H_{16})(\eta^5\text{-}C_6Me_6OH)][BF_4]$	6.84 (s, 4 H), 5.10 (s, 4 H)	3.24, 2.88 (AA'XX', 8 H)	3.72 (s, 3 H), 2.23 (s, 3 H), 1.99 (s, 6 H), 1.76 (s, 6 H)

Table 1 (*Continued*)

Compound	δ, J_{HH}/Hz		
	Cyclophane		
	Aromatic decks	Bridge	Cyclohexadienyl
14 $[Ru(\eta^6\text{-}C_{16}H_{16})(\eta^5\text{-}C_{16}H_{17})][BF_4]$	6.80 (s, 4 H), 5.14 (s, 4 H)	3.28, 2.92 (AA'XX', 8 H)	(Unco-ordinated ring H) 7.17, 6.95 (AB, 4 H, ^3J = 8.1) (Co-ordinated ring H) 4.33 (d, 2 H, ^3J = 7.3), 3.10 (t, 2 H, ^3J = 7.8) (Bridge) 3.22 (m, 2 H), 2.53 (t, 2 H, ^3J = 6.4), 2.45 (t, 2 H, ^3J = 7.4), 1.78 (t, 2 H, ^3J = 6.7) (Nucleophile) 3.28 (m, 1 H)

[a] In $CDCl_3$. s = Singlet, d = doublet, t = triplet, q = quartet, spt = septet and br = broad. [b] Coupling masked by overlapping signals from major isomer. [c] Solvent CD_3CN. [d] $[BPh_4]$: δ 6.99 (t, ^3J = 7.1, 4 H), 7.13 (t, ^3J = 7.6 Hz, 8 H) and 7.49 (br s, 8 H).

Table 2 Carbon-13 NMR data for selected compounds in $CDCl_3$

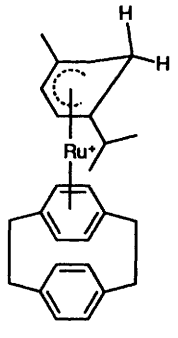
Compound	δ				
	Aryl C	Bridgehead	CH_2	Cyclohexadienyl	CN
3 $[Ru(\eta^6\text{-}C_{16}H_{16})(\eta^5\text{-}C_6H_6CN)][BF_4]$	133.9 87.7	139.8 127.5	34.0 32.1	89.5, 84.6, 32.8, 26.4	119.3
10 $[Ru(\eta^6\text{-}C_{16}H_{16})(\eta^5\text{-}C_6Me_6H)][BF_4]$	133.6 88.0	139.2 124.5	34.2 31.8	101.7, 100.5, 52.7, 38.4, 29.7, 18.1, 16.5, 16.0	
11* $[Ru(\eta^6\text{-}C_{16}H_{16})(\eta^5\text{-}C_6Me_6CN)][BF_4]$	133.8 89.3	139.1 126.6	34.1 31.7	99.9, 49.9, 21.1, 21.0, 17.0, 16.9	120.6

* Solvent CD_3CN.

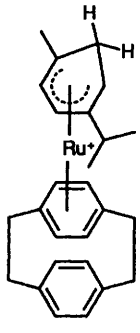
Table 3 Deuterium isotope shifts of $\nu(CH_{exo})$

Compound	$\nu(C\text{–}H_{exo})$/cm^{-1}	
	X = H	X = D
$[Ru(\eta^6\text{-}C_{16}H_{16})(\eta^5\text{-}C_6H_6X)][BF_4]$	2813	2113
$[Ru(\eta^6\text{-}C_{16}H_{16})(\eta^5\text{-}C_6Me_6X)][BF_4]$	2813	2107
$[Ru(\eta^6\text{-}C_{16}H_{16})(\eta^5\text{-}4\text{-}MeC_6H_4XCHMe_2)][BF_4]$*	2804	2129

* Signals for individual isomers unresolved.



6a



6b

strong bands at 2926 and 2813 cm^{-1} which may be assigned as $\nu(CH_{endo})$ and $\nu(CH_{exo})$ respectively.[10,13] A similar band is observed in the infrared spectrum of **3** at 2923 cm^{-1} but there are no bands in the ν(CH) region below 2850 cm^{-1}. The ^{13}C NMR spectrum of **3** (Table 2) displays a peak at δ 119.3 which is assigned as the resonance corresponding to the CN carbon atom. Treatment of **1** with $Na[BD_4]$ gives a product with a very similar ^1H NMR spectrum to **2** except for the absence of the doublet resonance at δ *ca.* 2. The infrared spectrum of this material displays $\nu(CH_{endo})$ at 2925 cm^{-1} but the band observed at 2813 cm^{-1} for **2** occurs at 2113 cm^{-1}, a typical deuterium isotope shift.[13,14] The reaction of $Na[BH_4]$ with $[Os(\eta^6\text{-}C_{16}H_{16})(\eta^6\text{-}C_6H_6)][BF_4]_2$[15] proceeds cleanly to give the analogous product $[Os(\eta^6\text{-}C_{16}H_{16})(\eta^5\text{-}C_6H_7)][BF_4]$ **4**, with no obvious decrease in rate in spite of the presumed lower electrophilicity of the osmium complex.[2] These results clearly indicate a single nucleophilic attack on the less-alkylated ring, to give a monocationic product with the added nucleophile in the *exo* position, an observation consistent with the rules of Davies *et al.*[16]

The action of $Na[BH_4]$ on the *p*-cymene complex $[Ru(\eta^6\text{-}C_{16}H_{16})(\eta^6\text{-}4\text{-}MeC_6H_4CHMe_2)][BF_4]_2$ **5**, however, gives two products, of the same empirical formula, in an approximate ratio of 5:2, which may be distinguished by their ^1H NMR spectra (Table 1). The infrared spectrum of these materials shows $\nu(CH_{endo})$ 2928 cm^{-1} and $\nu(CH_{exo})$ 2804 cm^{-1}. The two complexes were not separated but extensive decoupling experiments on the ^1H NMR spectrum of the mixture leads us to formulate these compounds as the two isomeric structures **6a** and **6b**. The major isomer, from the relative intensities in the ^1H NMR spectrum of the resonances due to the substituents on the cyclohexadienyl ring, is assigned the structure **6b**, with nucleophilic attack occurring at the site *ortho* to the methyl (as opposed to isopropyl) substituent.

An interesting feature of the ^1H NMR spectra of compounds **6a** and **6b** is that in each case the resonances corresponding to the four co-ordinated ring protons of the [2.2]paracyclophane ligand are not singlets as has been previously observed for metal–[2.2]paracyclophane complexes[10,15] but form a widely spaced AB pattern (δ 5.02 and 5.61 for the major isomer). The reason for this would appear to be the sensitivity of the [2.2]paracyclophane ligand to chirality at the metal centre[17] caused, for example, by the presence of three different ligands in addition to the cyclophane, co-ordinated to the ruthenium.

Recently it has been noted[18] that the presence of two different *ortho*-related substituents on a six-membered co-ordinated ring causes the formation of a chiral centre and is thus capable of rendering the cyclophane aromatic protons magnetically inequivalent in spite of the rapid rotation of the ligand. In these particular cases, **6a** and **6b**, either the isopropyl or methyl group is *ortho* to the attack site. In effect the alkyl substituent and the tetrahedral CH_2 group may be regarded as two very different ring sites and hence, due to the chirality when co-ordinated to a metal centre, cause a large splitting of the cyclophane resonances, as has been observed in other [2.2]-paracyclophane systems.[15]

The tetraphenylborate salts of these compounds were also prepared and their ^1H NMR spectra recorded. Surprisingly, while the general form of the spectrum remained the same, the coupling patterns were significantly more complex than those observed for the corresponding tetrafluoroborate salts. This is probably due to specific cation–anion interactions but the precise nature of the effects is unknown. The changes are consistent with those which occur on changing to a $[BPh_4]^-$ counter ion[15] in related chiral systems.

The reaction of compound **5** with KCN was also investigated and analogous products $[Ru(\eta^6\text{-}C_{16}H_{16})\{\eta^5\text{-}4\text{-}MeC_6H_4CHMe_2(CN)\}][BF_4]$, **7a** and **7b**, obtained in a similar isomer ratio, the most favourable site of attack again being the one *ortho* to the smaller (methyl) substituent. A steric dependence in the formation of isomers of this kind has also been observed in nucleophilic addition to cations of the type $[Mn(\eta^6\text{-}4\text{-}MeC_6H_4X)(CO)_3]^+$. The larger the substituent, X, the more nucleophilic attack is favoured *ortho* to the methyl group.[19] Parallel studies employing $Na[BD_4]$ gave the expected isotope shift, with $\nu(CD_{exo})$ appearing at 2129 cm^{-1}, confirming *exo* addition. The results of the deuteriation studies are summarised in Table 3.

The proposed structures for compounds **6a** and **6b** were further confirmed by an examination of the action of $Na[BH_4]$ on the 1,4-diisopropylbenzene derivative $[Ru(\eta^6\text{-}C_{16}H_{16})\{\eta^6\text{-}1,4\text{-}(Me_2CH)_2C_6H_4\}][BF_4]_2$ which was synthesised from 1,4-diisopropylbenzene and $[Ru(\eta^6\text{-}C_{16}H_{16})(OCMe_2)_3][BF_4]_2$ using the general method reported by Boekelheide and co-workers.[10] The product of this reaction, $[Ru(\eta^6\text{-}C_{16}H_{16})\{\eta^5\text{-}1,4\text{-}(Me_2CH)_2C_6H_5\}][BF_4]$ **8**, took the form of a single isomer and exhibited a ^1H NMR spectrum consistent with the expected single addition of hydride to the diisopropylbenzene ring. As in the case of **6a**,**6b** and **7a**,**7b** the proton resonances for the co-ordinated cyclophane deck took the form of an AB pattern (δ 5.04 and 5.59, ^3J = 6.3 Hz) indicating the presence of two different *ortho*-related substituents on the cyclohexadienyl ring, and the four methyl groups of the isopropyl substituents occurred as four separate doublet resonances (δ 1.04, 0.94, 0.92 and 0.80) indicating a unique environment for each substituent.

The reaction of $[Ru(\eta^6\text{-}C_{16}H_{16})(\eta^6\text{-}C_6Me_6)][BF_4]_2$ **9** with H^-, CN^- or OH^- under the conditions described above results in isolation of compounds of formulation $[Ru(\eta^6\text{-}C_{16}H_{16})(\eta^5\text{-}C_6Me_6X)][BF_4]$ (X = H **10**, CN **11** or OH **12**). Compound **10** displays a band in the infrared spectrum at $\nu(CH_{exo})$ 2813 cm^{-1}, which appears at 2107 cm^{-1} for the deuteriated analogue. This band is absent in the spectra of both **11** and **12**. The ^1H NMR spectrum of **10** (Table 1) clearly shows a quartet resonance (^3J = 6.7 Hz) for the added hydride (δ 2.00) and a corresponding methyl doublet at δ 1.01. The ^{13}C NMR spectrum of **11** displays a resonance at δ 120.6 corresponding to the CN carbon atom. For kinetically controlled reactions the rules of Davies *et al.*[16] predict attack at the less-alkylated ring (*i.e.* [2.2]paracyclophane), yet this is clearly not the case in this instance. This may be readily rationalised in terms of (*i*) the steric bulk of the [2.2]paracyclophane ligand, the unco-ordinated aromatic deck shielding the *exo* attack sites on the co-ordinated ring, and (*ii*) the deactivation of the co-ordinated deck of the cyclophane *via* π overlap with the unco-ordinated ring; interannular interactions within [2$_n$]cyclophanes are a well known phenomenon.[20–22]

Reduction of compound **9** with aluminium metal followed by protonation with HCl has been observed[10] to produce an isomer of **10** containing an η^5-cyclophane with the added proton in the *endo* position. In an attempt to examine the relative importance of the potential attack sites within the [2.2]paracyclophane ligand itself the action of $Na[BH_4]$ on $[Ru(\eta^6\text{-}C_{16}H_{16})_2][BF_4]_2$ **13** was examined. The reaction is not a clean one and proceeds with much decomposition and we were unable to isolate any pure product. However crude samples showed ^1H NMR spectra (Table 1) related to those observed by Boekelheide and co-workers,[10] consistent with a single *endo* addition of hydride to the more-alkylated bridgehead site of one of the co-ordinated aromatic decks to give a product $[Ru(\eta^6\text{-}C_{16}H_{16})(\eta^5\text{-}C_{16}H_{17})][BF_4]$ **14**. We would expect an *exo* attack at a non-bridgehead site, by the rules of Davies *et al.*[16] The reason for this surprising reactivity might well lie in the geometry of the co-ordinated cyclophane ligand which, in contrast to conventional η^6-arenes, is bent into a shallow boat conformation, the distortion being some 13° in the free ligand,[23] although this is reduced somewhat on co-ordination.[14] This results in the relevant molecular orbitals on the bridgehead atoms pointing outwards away from the metal ion and so an *endo* attack pathway could be less sterically unfavourable than in planar systems, especially since *exo* attack pathways are all blocked by the unco-ordinated deck of the [2.2]paracyclophane ligand.

Although it may seem surprising that reaction of $Na[BH_4]$ with these dications give monocationic, rather than a neutral, species, there is a well established precedent for such a reaction in (arene)ruthenium(II) chemistry,[24] where treatment of the mesitylene complex $[Ru(\eta^6\text{-}C_6H_3Me_3\text{-}1,3,5)(PMe_2Ph)(phen)][PF_6]_2$ (phen = 1,10-phenanthroline) with $Na[BH_4]$ in methanol gives $[Ru(\eta^5\text{-}C_6H_4Me_3)(PMe_2Ph)(phen)][PF_6]$. Similarly $[Fe(\eta^6\text{-}C_6H_3Me_3\text{-}1,3,5)_2]^{2+}$ reacts with KCN in acetone to form $[Fe(\eta^6\text{-}C_6H_3Me_3\text{-}1,3,5)\{\eta^5\text{-}C_6H_3Me_3(CN)\}]^+$.[25] Conversely, reactions of various $[Ru(\eta^6\text{-arene})_2]^{2+}$ ions with $Na[BH_4]$ in anhydrous tetrahydrofuran (thf) are consistent with the exclusive formation of neutral arene–cyclohexadiene complexes in high yield although it was noted that in water low yields of monocationic arene–cyclohexadienyl complexes were obtained.[26] It has also been noted that reaction of $[Fe(\eta^6\text{-}C_6Me_6)_2]^{2+}$ with LiMe will give both η^5 and η^4 products, depending upon the precise reaction conditions employed.[27] Hence it seems likely that the choice of methanol as a solvent for this study is responsible for the observation of only single hydride attack, leading to the formation of monocationic products.

We intend to carry out further studies into nucleophilic attack on co-ordinated [2,2]paracyclophane and related ligands as well as on the more highly charged bi- and tri-nuclear 'cylinder complexes' in which both decks of the cyclophane ligands are complexed.[10,28]

Experimental

Instrumental.—The IR spectra were recorded on a PE983 grating spectrometer between 4000 and 200 cm^{-1} as either KBr disks or Nujol mulls on CsI plates, NMR spectra on either Varian XL200 or VXR400 spectrometers. Microanalyses were carried out by the departmental service at University College London. All manipulations were carried out under nitrogen with degassed solvents using conventional Schlenk-line techniques.

Starting Materials.—The compounds $[M(\eta^6\text{-}C_{16}H_{16})(\eta^6\text{-arene})][BF_4]_2$ (M = Ru or Os) were prepared by published literature methods[4,28–30] or simple modifications thereof. Ruthenium trichloride hydrate and sodium hexachloroosmate were obtained on loan from Johnson Matthey plc and all other

reagents and materials were obtained from the usual commercial sources.

Preparations.—$[Ru(\eta^6\text{-}C_{16}H_{16})(\eta^5\text{-}C_6H_7)][BF_4]$ **2**. The compound $[Ru(\eta^6\text{-}C_{16}H_{16})(\eta^6\text{-}C_6H_6)][BF_4]_2$ (0.107 g, 0.191 mmol) was suspended in methanol (5 cm^3) and to the stirred mixture excess of $Na[BH_4]$ (0.05 g) was gradually added over 15 min during which time a rapid colour change from yellow to deep green was observed. Water (5 cm^3) was added to destroy any remaining $Na[BH_4]$ and the mixture was extracted with one aliquot of dichloromethane (20 cm^3). The separated organic layer was dried over magnesium sulfate, filtered and evaporated to dryness. The residue was recrystallised from acetone, isolated by filtration and washed with a few drops of acetone and diethyl ether to give a pale yellow product. Yield 0.037 g, 41% (Found: C, 55.10; H, 4.35. Calc. for $C_{22}H_{23}BF_4Ru$: C, 55.60; H, 4.90%).

$[Ru(\eta^6\text{-}C_{16}H_{16})(\eta^5\text{-}C_6H_6CN)][BF_4]$ **3**. The compound $[Ru(\eta^6\text{-}C_{16}H_{16})(\eta^6\text{-}C_6H_6)][BF_4]_2$ (0.098 g, 0.175 mmol) was suspended in methanol (5 cm^3) and KCN (0.012 g, 0.184 mmol) added. The mixture was stirred for 15 min until a bright yellow solution was obtained. The mixture was filtered and diethyl ether added to give a pale yellow precipitate. This was filtered off and the residue dissolved in dichloromethane (5 cm^3). After further filtration the solution was evaporated to dryness to give a bright yellow product. Yield 0.054 g, 65% (Found: C, 54.85; H, 4.70; N, 2.40. Calc. for $C_{23}H_{22}BF_4NRu$: C, 55.20; H, 4.45; N, 2.80%).

$[Os(\eta^6\text{-}C_{16}H_{16})(\eta^6\text{-}C_6H_7)][BF_4]$ **4**. Using an analogous method to that for compound **2**, $[Os(\eta^6\text{-}C_{16}H_{16})(\eta^6\text{-}C_6H_6)][BF_4]_2$ (0.068 g, 0.105 mmol) was treated with $Na[BH_4]$ to give an off-white solid. Yield 0.028 g, 48% (Found: C, 46.85; H, 3.85. Calc. for $C_{22}H_{23}BF_4Os$: C, 46.80; H, 4.10%).

$[Ru(\eta^6\text{-}C_{16}H_{16})(\eta^5\text{-}C_6Me_6H)][BF_4]$ **10**. Using an analogous method to that for compound **2**, $[Ru(\eta^6\text{-}C_{16}H_{16})(\eta^6\text{-}C_6Me_6)][BF_4]_2$ (0.102 g, 0.159 mmol) was treated with $Na[BH_4]$ to give a yellow solid. Yield 0.036 g, 41% (Found: C, 59.95; H, 6.10. Calc. for $C_{28}H_{35}BF_4Ru$: C, 60.10; H, 6.30%).

$[Ru(\eta^6\text{-}C_{16}H_{16})(\eta^5\text{-}4\text{-}MeC_6H_5CHMe_2)][BF_4]$ **6a** *and* **6b**. Using an analogous method to that for compound **2**, $[Ru(\eta^6\text{-}C_{16}H_{16})(\eta^6\text{-}4\text{-}MeC_6H_4CHMe_2)][BF_4]_2$ (0.137 g, 0.223 mmol) was treated with $Na[BH_4]$ to give a yellow solid containing two isomers, **6a**:**6b** 2:5 (NMR evidence). Yield 0.069 g, 59% (Found: C, 58.95; H, 5.80. Calc. for $C_{26}H_{31}BF_4Ru$: C, 58.80; H, 5.90%).

$[Ru(\eta^6\text{-}C_{16}H_{16})(\eta^5\text{-}4\text{-}MeC_6H_5CHMe_2)][BPh_4]$. To a solution of compound **6** (0.074 g, 0.139 mmol) in methanol (3 cm^3) was added a solution containing an excess of sodium tetraphenylborate (0.1 g) in methanol (3 cm^3). The yellow product was filtered off, washed with methanol and diethyl ether, and air dried. Yield 0.100 g, 94% (Found: C, 78.40; H, 6.75. Calc. for $C_{50}H_{51}BRu$: C, 78.60; H, 6.70%).

$[Ru(\eta^6\text{-}C_{16}H_{16})(\eta^5\text{-}C_6Me_6CN)][BF_4]$ **11**. The compound $[Ru(\eta^6\text{-}C_{16}H_{16})(\eta^6\text{-}C_6Me_6)][BF_4]_2$ (0.099 g, 0.154 mmol) was suspended in methanol (5 cm^3) and KCN (0.0133 g, 0.204 mmol) added. The mixture was stirred for 15 min until a bright yellow solution was obtained. It was filtered and diethyl ether added to precipitate a pale yellow solid. The solid was filtered off and then extracted with dichloromethane (5 cm^3). Filtration of this solution followed by evaporation gave a bright yellow product. Yield 0.030 g, 34% (Found: C, 59.65; H, 6.05; N, 2.70. Calc. for $C_{29}H_{34}BF_4Ru$: C, 59.60; H, 5.85; N, 2.40%).

$[Ru(\eta^6\text{-}C_{16}H_{16})(\eta^5\text{-}4\text{-}MeC_6H_4CHMe_2CN)][BF_4]$ **7a** *and* **7b**. Using the method described for compound **11**, $[Ru(\eta^6\text{-}C_{16}H_{16})(\eta^6\text{-}4\text{-}MeC_6H_4CHMe_2)][BF_4]_2$ (0.136 g, 0.221 mmol) was treated with KCN to give an off-white product consisting of two isomers **7a**:**7b** 2:5 (NMR evidence). Yield 0.067 g, 54% (Found: C, 57.75; H, 5.30; N, 2.50. Calc. for $C_{27}H_{30}BF_4NRu$: C, 58.30; H, 5.45; N, 2.50%).

$[Ru(\eta^6\text{-}C_{16}H_{16})\{\eta^5\text{-}1,4\text{-}(Me_2CH)_2C_6H_5\}][BF_4]$ **8**. Using a similar method to that described for compound **2**, $[Ru(\eta^6\text{-}C_{16}H_{16})\{\eta^6\text{-}1,4\text{-}(Me_2CH)_2C_6H_4\}][BF_4]_2$ (0.345 g, 0.0535 mmol) was treated with $Na[BH_4]$ to give a yellow solid. Yield 0.072 g, 24% (Found: C, 60.30; H, 6.25. Calc. for $C_{28}H_{35}BF_4Ru$: C, 60.10; H, 6.30%).

$[Ru(\eta^6\text{-}C_{16}H_{16})(\eta^5\text{-}C_6Me_6OH)][BF_4]$ **12**. Using a similar method to that described for compound **11**, $[Ru(\eta^6\text{-}C_{16}H_{16})(\eta^6\text{-}C_6Me_6)][BF_4]_2$ (0.053 g, 0.0821 mmol) was treated with sodium hydroxide (0.001 g, 0.125 mmol) to give an orange product. Yield 0.022 g, 47% (Found: C, 59.15; H, 6.00. Calc. for $C_{28}H_{35}BF_4ORu$: C, 58.45; H, 6.15%).

The deuterides of compounds **2**, **6** and **10** were prepared in an identical fashion to their undeuteriated counterparts substituting $Na[BD_4]$ for $Na[BH_4]$ (Found: C, 55.50; H, 5.00. Calc. for $C_{22}H_{22}BDF_4Ru$ **2′**: C, 55.50; H, 5.10. Found: C, 59.70; H, 6.00. Calc. for $C_{26}H_{30}BDF_4Ru$ **6′**: C, 60.00; H, 6.50. Found: C, 58.60; H, 5.85. Calc. for $C_{28}H_{34}BDF_4Ru$ **10′**: C, 58.65; H, 6.05%).

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