Sterically Controlled Double Nucleophilic Addition Reactions of (η^6-Arene)(η^6-[2.2]paracyclophane)ruthenium(II) Complexes and Reactions to form Highly Fluxional Agostic Cyclohexenyls

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Action of the hydride source $Na[BH_4]$ on the (η^6-arene)(η^6-[2.2]paracyclophane)ruthenium(II) complexes $[Ru(\eta^6\text{-}C_{16}H_{16})(\eta^6\text{-arene})][BF_4]_2$ (arene = benzene **1a**, *p*-cymene **1b**, 1,2,4,5-tetramethylbenzene **1c**, pentamethylbenzene **1d** or hexamethylbenzene **1e**) results exclusively in the addition of two hydride nucleophiles to the non-cyclophane arene ring, giving the neutral (1,3-diene)ruthenium(0) complexes $[Ru(\eta^6\text{-}C_{16}H_{16})(\eta^4\text{-diene})]$ (diene = $C_6Me_6H_2$ **4**, $C_6Me_5H_3$ **6**, $C_6Me_4H_4$ **7** or $MeC_6H_6CHMe_2$ **8**). Complex **4** is the 1,3-diene isomer of the previously reported 1,4-diene compound $[Ru(\eta^6\text{-}C_{16}H_{16})(\eta^4\text{-}3,6\text{-}C_6Me_6H_2)]$ **2** (formed in the reduction of **1e** by Red-Al $\{Na[AlH_2(OCH_2CH_2OMe)_2]\}$). In complexes **1a–1e**, attack on the [2.2]paracyclophane ligand is not observed, implying that nucleophilic additions to these compounds are not charge controlled. This contrasts with previously reported related reactions which give bis(cyclohexadienyl) complexes. Attempts to prepare functionalised diene complexes derived from **1a** and **1e** were largely unsuccessful although the functionalised cyclohexadienyl compounds $[Ru(\eta^6\text{-}C_{16}H_{16})(\eta^5\text{-}C_6R_6X)][BF_4]$ **9–11** (R = H or Me; X = Me or OMe) are prepared. Deprotonation of the hexamethylbenzene complex **1e** results in the formation of the *exo*-methylene species $[Ru(\eta^6\text{-}C_{16}H_{16})\{\eta^5\text{-}C_6Me_5(CH_2)\}][BF_4]$ **12** and $[Ru(\eta^6\text{-}C_{16}H_{16})\{\eta^4\text{-}C_6Me_4(CH_2)_2\}]$ **13**. Complexes **4**, **6** and **7** react with HBF_4 to generate agostic cyclohexenyl compounds $[Ru(\eta^6\text{-}C_{16}H_{16})(\eta^3\text{-}C_6Me_nH_{9-n})][BF_4]$ (n = 6 **16**, 5 **20** or 4 **21**). However, reaction of **2** with HBF_4 gives the exocyclic agostic complex $[Ru(\eta^6\text{-}C_{16}H_{16})\{\eta^3\text{-}(HCH_2)(CH_2)C_6Me_4H_4\}][BF_4]$ **18**. In **16** the agostic cyclohexenyl ligand is bound *via* an endocyclic allylic functionality whereas in the isomer, **18**, the metal is bound externally to the ring. Deprotonation of **18** with $LiBu^n$ results in the abstraction of the agostic proton to generate $[Ru(\eta^6\text{-}C_{16}H_{16})\{\eta^4\text{-}(CH_2)_2C_6Me_4H_4\}]$ **19**, which is isomeric with **2** and **4** and contains a saturated $C_6Me_4H_4(CH_2)_2$ ring bound to the metal centre by two exocyclic olefinic functionalities. The mechanisms for the formation of these compounds have been probed by deuteriation studies and their extensive dynamic behaviour investigated by variable-temperature ^1H NMR spectroscopy.

Nucleophilic addition reactions to co-ordinated arene rings are of significant interest and practical viability in arene and diene functionalisation.[1–5] Bis(arene) complexes of ruthenium(II) are of especial relevance in this context because of their high stability and lack of air and moisture sensitivity. Although somewhat less electrophilic than their iron analogues,[6] the ruthenium compounds are less prone to decomposition arising from the competing formation of unstable 19 and 20 electron species, on reaction with carbon donor nucleophiles.[1,5] Moreover, a wide range of unsymmetrical bis(arene)ruthenium complexes are available *via* the routes of Bennett and Matheson[7] and Rybinskaya *et al.*[8] unlike the iron analogues.

Single nucleophilic addition reactions give rise to functionalised cyclohexadienyl complexes[9–12] from which functionalised arenes may be generated by hydride abstraction.[13,14] Double nucleophilic additions to $[Ru(\eta^6\text{-arene})_2]^{2+}$ species can, in principle, give useful functionally disubstituted 1,3- or 1,4-cyclohexadiene complexes of Ru^0. In practice however, all nucleophilic additions so far studied, except some reactions with hydride ions,[15,16] give rise to bis(cyclohexadienyl) complexes even when one of the arenes is the sterically congested 1,3,5-tris(isopropyl)benzene ligand.[5]

Recently, we have shown that the steric properties of the polyaromatic [2.2]paracyclophane ligand are suitable for inducing single nucleophilic addition reactions at other arenes co-ordinated to the same metal centre, even in the case of poorly electrophilic arenes such as hexamethylbenzene.[17,18] It is also noteworthy that Boekelheide and co-workers[19] have demonstrated that the action of the hydride source Red-Al $\{Na[AlH_2(OCH_2CH_2OMe)_2]\}$ upon $[Ru(\eta^6\text{-}C_{16}H_{16})(\eta^6\text{-arene})][BF_4]_2$ (arene = C_6H_6 **1a** or C_6Me_6 **1e**) gives solely diene products.

We now present the results of our investigations into the formation of (diene)ruthenium(0) complexes from double nucleophilic addition reactions of (arene)ruthenium(II) complexes containing [2.2]paracyclophane as a non-innocent spectator ligand. The reactivity of the resulting products towards HBF_4 is also investigated. A preliminary report of part of this work has already been published.[20]

Experimental

Instrumental.—Infrared spectra were recorded on a PE983 spectrometer between 4000 and 180 cm^{-1} as either KBr disks or Nujol mulls on CsI plates. NMR spectra were recorded on a Varian VXR400 spectrometer at University College London and microanalyses were carried out by the departmental service. Fast atom bombardment (FAB) mass spectra were recorded by the University of London Intercollegiate Research Service at the School of Pharmacy. All manipulations were carried out under nitrogen with dried, degassed solvents using conventional Schlenk-line techniques.

Starting Materials.—$[Ru(\eta^6\text{-}C_{16}H_{16})(\eta^6\text{-arene})][BF_4]_2$ complexes were prepared by published literature methods[7,19] from the appropriate dichloride dimer $[\{Ru(\eta^6\text{-arene})Cl(\mu\text{-}$

Cl)}$_2$].[21] Ruthenium trichloride hydrate was obtained on loan from Johnson Matthey and was purified before use by repeated dissolution in water and boiling to dryness. All other reagents and materials were obtained from the usual commercial sources.

Preparations.—[Ru(η^6-$C_{16}H_{16}$)(η^4-$C_6H_6D_2$)] **3'**. The compound [Ru(η^6-$C_{16}H_{16}$)(η^6-C_6H_6)][BF_4]$_2$ (0.15 g, 0.27 mmol) was suspended in tetrahydrofuran (thf) with Na[BD_4] (0.05 g, excess) and the mixture stirred for 4 h. The solvent was removed *in vacuo* and the product extracted into hexane (2 × 20 cm^3) and filtered. Slow evaporation of the filtrate and cooling resulted in the formation of the product as air-sensitive yellow microcrystals. Yield 0.06 g, 0.15 mmol, 56% (Found: C, 68.35; H, 6.30. Calc. for $C_{22}H_{24}D_2Ru$: C, 67.50; H, 6.70%). The identity of the complex was confirmed by ^{1}H NMR spectroscopy by comparison with a sample of the undeuteriated counterpart [Ru(η^6-$C_{16}H_{16}$)(η^4-C_6H_8)] **3**.[19]

[Ru(η^6-$C_{16}H_{16}$)(η^4-5,6-$C_6Me_6H_2$)] **4**. The compound [Ru(η^6-$C_{16}H_{16}$)(η^6-C_6Me_6)][BF_4]$_2$ (0.09 g, 0.15 mmol) was stirred in thf (10 cm^3) for 4 d with Na[BH_4] (0.05 g, excess). Water (0.5 cm^3) was added to destroy the excess reducing agent and the mixture evaporated to dryness. The resulting yellow residue was extracted into hexane (40 cm^3) and filtered. Slow evaporation of the yellow filtrate and cooling gave the product as bright mildly air-sensitive yellow crystals. Yield 0.04 g, 0.08 mmol, 53% (Found: C, 70.50; H, 7.85. Calc. for $C_{28}H_{36}Ru$: C, 71.00; H, 7.65%).

[Ru(η^6-$C_{16}H_{16}$)(1-σ:3-5-η-$C_6Me_6H_2$)] **5**. Treatment of the compound [Ru(η^6-$C_{16}H_{16}$)(η^6-C_6Me_6)][BF_4]$_2$ (0.12 g, 0.19 mmol) in thf (10 cm^3) with Red-Al–toluene (0.5 cm^3, 3.4 mol dm^{-3}, 1.7 mmol) as previously described[19] followed by evaporation of the solvents, extraction into hexane (2 × 20 cm^3) and pumping to dryness resulted in the isolation of a 67:8:25 mixture of complexes **2**, **4** and **5** respectively. Compound **5** was not isolated in pure form.

[Ru(η^6-$C_{16}H_{16}$)(η^4-$C_6Me_5H_3$)] **6**. The compound [Ru(η^6-$C_{16}H_{16}$)(η^6-C_6Me_5H)][BF_4]$_2$ (0.13 g, 0.20 mmol) was treated with Na[BH_4] (0.05 g) as described for **4**. Extraction into hexane (40 cm^3) followed by removal of the solvent *in vacuo* resulted in the deposition of the product as a mildly air-sensitive yellow powder. Yield 0.05 g, 0.12 mmol, 60% (Found: C, 71.15; H, 7.70. Calc. for $C_{27}H_{34}Ru$: C, 70.55; H, 7.45%).

[Ru(η^6-$C_{16}H_{16}$)(η^4-$C_6Me_4H_4$)] **7**. The compound [Ru(η^6-$C_{16}H_{16}$)(η^6-$C_6Me_4H_2$)][BF_4]$_2$ (0.10 g, 0.16 mmol) was treated with Na[BH_4] (0.05 g) as described for **4**. Extraction into hexane followed by removal of the solvent *in vacuo* resulted in the deposition of the product as an air-sensitive yellow powder contaminated with *ca.* 20% free [2.2]paracyclophane. Removal of free ligand by sublimation under vacuum at 100 °C followed by recrystallisation from hexane gave the pure product. Yield 0.03 g, 0.09 mmol, 56% (Found: C, 71.05; H, 7.40. Calc. for $C_{26}H_{32}Ru$: C, 70.10; H, 7.25%).

[Ru(η^6-$C_{16}H_{16}$){η^4-1-(CHMe$_2$)-4-MeC_6H_6}] **8a**. The compound [Ru(η^6-$C_{16}H_{16}$)(η^6-*p*-MeC_6H_4CHMe$_2$)][BF_4]$_2$ (0.27 g, 0.44 mmol) was treated with Na[BH_4] (0.10 g) over a period of 24 h in a similar manner to that described for **4**. Extraction into hexane without addition of water, followed by removal of the solvent *in vacuo* resulted in the deposition of the product as an air-sensitive yellow powder. Yield 0.10 g, 0.22 mmol, 50% (Found: C, 71.85; H, 7.45. Calc. for $C_{26}H_{32}Ru$: C, 70.10; H, 7.25%).* An identical product was obtained from the analogous reduction with Red-Al, which was carried out as previously described for **3**.[19]

[Ru(η^6-$C_{16}H_{16}$){η^4-2-(CHMe$_2$)-5-MeC_6H_6}] **8b**. The compound [Ru(η^6-$C_{16}H_{16}$)(η^6-*p*-MeC_6H_4CHMe$_2$)][BF_4]$_2$ (0.10 g, 0.16 mmol) was treated with Na[BH_4] (0.05 g) over a period of 24 h in a similar manner to that described for **4**. Quenching with water (0.5 cm^3), extraction into hexane (2 × 20 cm^3), followed by removal of the solvent *in vacuo*, resulted in the deposition of the product as an air-sensitive yellow powder. Yield 0.05 g, 0.11 mmol, 68% (Found: C, 72.25; H, 7.90. Calc. for $C_{26}H_{32}Ru$: C, 70.10; H, 7.25%).*

[Ru(η^6-$C_{16}H_{16}$)(η^5-C_6Me_7)][BF_4] **9**. The compound [Ru(η^6-$C_{16}H_{16}$)(η^6-C_6Me_6)][BF_4]$_2$ (0.17 g, 0.26 mmol) was stirred in thf (10 cm^3) for 1 h with LiMe–Et_2O (1.6 mol dm^{-3}, 1 cm^3) at −78 °C. The resulting bright yellow-orange suspension was allowed to warm slowly to room temperature and was stirred for a further 1 h. A further aliquot of LiMe–Et_2O was added (1 cm^3) such that the solution became clear orange. Degassed water (5 cm^3) was added to destroy the excess alkylating reagent and the organic layer separated. The aqueous phase was washed with a further portion of CH_2Cl_2 (5 cm^3) and the washings combined with the organic phase and dried over $MgSO_4$. After removal of solvent *in vacuo* the yellow oily residue was triturated with Et_2O (10 cm^3) to give the product as an air-stable yellow solid. Yield 0.07 g, 0.12 mmol, 46% (Found: C, 59.50; H, 6.35. Calc. for $C_{29}H_{37}BF_4Ru$: C, 60.75; H, 6.50%).†

[Ru(η^6-$C_{16}H_{16}$)(η^5-C_6H_6OMe)][BF_4] **11**. The compound [Ru(η^6-$C_{16}H_{16}$)(η^6-C_6H_6)][BF_4]$_2$ (0.13 g, 0.24 mmol) was stirred in MeOH (5 cm^3) while LiMe–Et_2O (1.6 mol dm^{-3}, 1 cm^3) was added dropwise over a period of *ca.* 5 min. The resulting yellow solution was evaporated to *ca.* 1 cm^3 resulting in the deposition of the product as air-stable orange crystals. Yield 0.11 g, 0.21 mmol, 88% (Found: C, 54.25; H, 5.35. Calc. for $C_{23}H_{25}BF_4ORu$: C, 54.65; H, 5.00%).

[Ru(η^6-$C_{16}H_{16}$){η^5-$C_6Me_5(CH_2)$}][BF_4] **12**. The compound [Ru(η^6-$C_{16}H_{16}$)(η^6-C_6Me_6)][BF_4]$_2$ (0.08 g, 0.12 mmol) was stirred in MeOH (5 cm^3) while LiBu^n–Et_2O (1.6 mol dm^{-3}, 1 cm^3) was added dropwise over a period of *ca.* 5 min. The resulting yellow solution was evaporated to *ca.* 1 cm^3 resulting in the deposition of the product as air-stable yellow crystals. Yield 0.05 g, 0.09 mmol, 75% (Found: C, 60.05; H, 5.90. Calc. for $C_{28}H_{33}BF_4Ru$: C, 60.35; H, 5.95%). This compound may also be prepared in lower yield by reaction of **1e** with a single molar equivalent of KOBu^t in dry thf.

[Ru(η^6-$C_{16}H_{16}$){η^4-$C_6Me_4(CH_2)_2$}] **13**. The compound [Ru(η^6-$C_{16}H_{16}$)(η^6-C_6Me_6)][BF_4]$_2$ (0.17 g, 0.27 mmol) was stirred in thf (10 cm^3) with KOBu^t–Bu^{t}OH (1.0 cm^3, 1.0 mol dm^{-3}) for 4 h. The resulting bright yellow solution was evaporated to dryness and extracted into warm hexane (2 × 40 cm^3). The solution was filtered and evaporated to dryness. Recrystallisation from acetone gave the product as mildly air-sensitive yellow crystals. Yield 0.12 g, 0.26 mmol, 96% (Found: C, 71.00; H, 6.95. Calc. for $C_{28}H_{32}Ru$: C, 71.60; H, 6.85%).

[Ru(η^6-$C_{16}H_{16}$)(η^3-$C_6Me_6H_3$)][BF_4] **16**. To a hexane (30 cm^3) solution of [Ru(η^6-$C_{16}H_{16}$)(η^4-5,6-$C_6Me_6H_2$)] **4** prepared from [Ru(η^6-$C_{16}H_{16}$)(η^6-C_6Me_6)][BF_4]$_2$ **1e** (0.19 g, 0.30 mmol) was added HBF_4 (0.2 cm^3, 40% aq.) and the mixture stirred vigorously for 1 h. The colourless organic layer was decanted off and the aqueous layer washed with diethyl ether to give the product as the pale yellow monohydrate which was isolated by filtration and air dried. Yield 0.08 g, 0.13 mmol,

* The product **8a** was shown by ^{1}H NMR to be contaminated by *ca.* 20% free [2.2]paracyclophane, analogously *ca.* 25% in the case of **8b**. Attempts to remove this impurity by sublimation were unsuccessful because of decomposition of the complex at higher temperatures, which generated additional free cyclophane impurity. Chromatographic separation was ruled out because of the high air sensitivity of the complexes. Similar problems were found in the case of **3**[19] (Recalc. for $C_{26}H_{32}Ru$·0.2$C_{16}H_{16}$ **8a**: C, 72.00; H, 7.30. Recalc. for $C_{26}H_{32}$-Ru·0.25$C_{16}H_{16}$ **8b**: C, 72.40; H, 7.30%). The formulation of both complexes was confirmed by FAB mass spectra. In each case molecular ion peaks were observed at *m/z* 446 (based on ^{102}Ru) with little fragmentation.

† The poor analytical data for this compound is probably due to contamination by traces of lithium salts which could not be separated because of the high solubility of the complex. FAB mass spectral data clearly establish the proposed formulation however, with a molecular cation peak at *m/z* 487 (based on ^{102}Ru) and a strong peak corresponding to the C_6Me_7 ligand, *m/z* 177.

43% based on **1e** (Found: C, 57.75; H, 6.50. Calc. for $C_{28}H_{37}BF_4Ru{\cdot}H_2O$:* C, 58.05; H, 6.80%).

$[Ru(\eta^6\text{-}C_{16}H_{16})(\eta^3\text{-}C_6Me_6H_2D)][BF_4]$ **16**″. To a hexane (30 cm^3) solution of $[Ru(\eta^6\text{-}C_{16}H_{16})(\eta^4\text{-}5,6\text{-}C_6Me_6H_2)]$ **4** prepared from $[Ru(\eta^6\text{-}C_{16}H_{16})(\eta^6\text{-}C_6Me_6)][BF_4]_2$ **1e** (0.16 g, 0.24 mmol) was added a pre-mixed solution of HBF_4 (0.1 cm^3, aq., 40%)–D_2O (1 cm^3) and the mixture stirred vigorously for 7 d. The product was isolated as described for **16**. Yield 0.08 g, 0.14 mmol, 58% based on **1e** (Found: C, 58.60; H, 6.55. Calc. for $C_{28}H_{36}DBF_4Ru{\cdot}H_2O$:* C, 57.95; H, 6.95%).

$[Ru(\eta^6\text{-}C_{16}H_{16})(\eta^3\text{-}C_6Me_6H_2D)][H(O_2CCF_3)_2]$ **17**. To a hexane (30 cm^3) solution of $[Ru(\eta^6\text{-}C_{16}H_{16})(\eta^4\text{-}5,6\text{-}C_6Me_6H_2)]$ **4** prepared from $[Ru(\eta^6\text{-}C_{16}H_{16})(\eta^6\text{-}C_6Me_6)][BF_4]_2$ **1e** (0.11 g, 0.17 mmol) was added CF_3CO_2D (0.2 cm^3) and the mixture stirred for 15 min. The colourless organic layer was decanted off and the yellow acid layer stirred with diethyl ether (10 cm^3) to give the product as yellow crystals. Yield 0.06 g, 0.09 mmol, 53% based on **1e** (Found: C, 54.50; H, 5.15. Calc. for $C_{32}H_{37}DF_6O_4Ru$: C, 54.70; H, 5.60%).

$[Ru(\eta^6\text{-}C_{16}H_{16})\{\eta^3\text{-}(HCH_2)(CH_2)C_6Me_4H_4\}][BF_4]$ **18**. To a hexane (30 cm^3) solution of $[Ru(\eta^6\text{-}C_{16}H_{16})(\eta^4\text{-}3,6\text{-}C_6Me_6H_2)]$ **2** (0.11 g, 0.23 mmol) prepared as previously reported[19] was added $HBF_4{\cdot}Et_2O$ (0.05 cm^3, 54%) and the mixture stirred for 20 min resulting in the deposition of the product as a pale yellow monohydrate. Yield 0.10 g, 0.17 mmol, 74% (Found: C, 58.50; H, 6.55. Calc. for $C_{28}H_{37}BF_4Ru{\cdot}H_2O$:* C, 58.05; H, 6.80%). The same product is also obtained less cleanly from the analogous reaction with aqueous HBF_4.

$[Ru(\eta^6\text{-}C_{16}H_{16})\{\eta^4\text{-}(CH_2)_2C_6Me_4H_4\}]$ **19**. To a thf (30 cm^3) solution of $[Ru(\eta^6\text{-}C_{16}H_{16})\{\eta^3\text{-}(HCH_2)(CH_2)C_6Me_4H_4\}][BF_4]$ **18** (0.05 g, 0.09 mmol) was added $LiBu^n$–hexane (0.1 cm^3, 1.6 mol dm^{-3}, 0.16 mmol) initially at −80 °C. The mixture was stirred and allowed to warm to room temperature over a period of *ca.* 20 min resulting in the formation of a bright yellow solution and a small quantity of a fine brown precipitate. Water (0.2 cm^3) was added to destroy unreacted $LiBu^n$ and the mixture evaporated to dryness. The product was extracted with hexane (2 × 20 cm^3) and the solvent removed *in vacuo* resulting in the formation of a yellow oil from which bright yellow crystals were deposited. Yield 0.04 g, 0.08 mmol, 89% (Found: C, 71.05; H, 7.95. Calc. for $C_{28}H_{36}Ru$: C, 71.00; H, 7.65%).

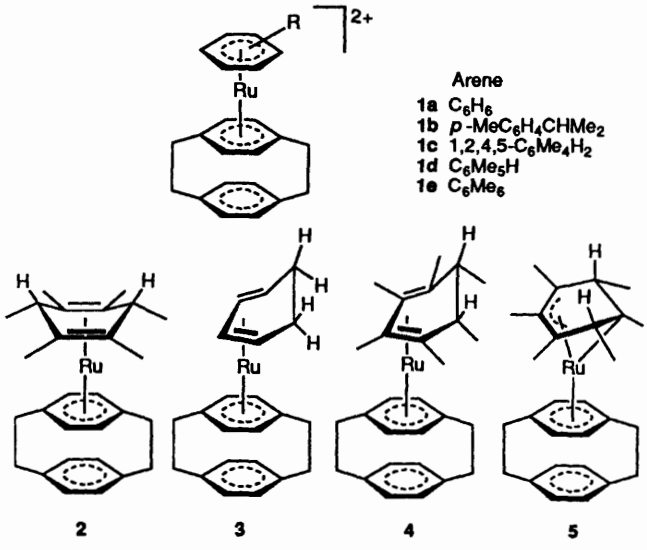
$[Ru(\eta^6\text{-}C_{16}H_{16})(\eta^3\text{-}C_6Me_5H_4)][BF_4]$ **20**. A hexane (30 cm^3) solution of $[Ru(\eta^6\text{-}C_{16}H_{16})(\eta^4\text{-}C_6Me_5H_3)]$ **6** prepared from $[Ru(\eta^6\text{-}C_{16}H_{16})(\eta^6\text{-}C_6Me_5H)][BF_4]_2$ **1d** (0.10 g, 0.15 mmol) was treated with HBF_4 (0.2 cm^3, 40% aq.) as described for **16**. Yield 0.03 g, 0.05 mmol, 33% based on **1d** (Found: C, 58.25; H, 6.50. Calc. for $C_{27}H_{35}BF_4Ru{\cdot}0.5H_2O$:* C, 58.30; H, 6.50%).

$[Ru(\eta^6\text{-}C_{16}H_{16})(\eta^3\text{-}C_6Me_4H_5)][BF_4]$ **21**. A diethyl ether (30 cm^3) solution of $[Ru(\eta^6\text{-}C_{16}H_{16})(\eta^4\text{-}C_6Me_4H_4)]$ **7** prepared from $[Ru(\eta^6\text{-}C_{16}H_{16})(\eta^6\text{-}C_6Me_4H_2)][BF_4]_2$ **1c** (0.11 g, 0.17 mmol) was treated with $HBF_4{\cdot}Et_2O$ (0.1 cm^3, 54%) and the mixture stirred for 20 min resulting in the deposition of a grey precipitate. Recrystallisation from chloroform–diethyl ether, liquid–vapour diffusion gave the product as feathery yellow crystals. Yield 0.04 g, 0.07 mmol, 41% based on **1c** (Found: C, 56.50; H, 5.65. Calc. for $C_{26}H_{33}BF_4Ru{\cdot}H_2O$:* C, 56.65; H, 6.40%).

The deuterides of compounds **4**, **6** and **16** were prepared in an identical fashion to their undeuteriated counterparts substituting $Na[BD_4]$ for $Na[BH_4]$ in the procedure, and their identities confirmed by infrared and ^1H NMR spectroscopy (Found: C, 71.35; H, 8.25. Calc. for $C_{28}H_{34}D_2Ru$ **4**′: C, 70.70; H, 8.05. Found: C, 69.35; H, 7.95. Calc. for $C_{27}H_{32}D_2Ru$ **6**′: C, 70.25; H, 7.86. Found: C, 58.40; H, 6.20. Calc. for $C_{28}H_{35}D_2BF_4Ru{\cdot}H_2O$ **16**′:* C, 57.85; H, 7.11%).

Results and Discussion

(Diene)ruthenium(0) Complexes.—Work by Boekelheide and co-workers[19] has shown that the reduction of the hexamethylbenzene complex $[Ru(\eta^6\text{-}C_{16}H_{16})(\eta^6\text{-}C_6Me_6)][BF_4]_2$ **1e** with Red-Al [sodium bis(methoxyethoxy) aluminium hydride] gives the cyclohexa-1,4-diene ruthenium(0) compound $[Ru(\eta^6\text{-}C_{16}H_{16})(\eta^4\text{-}exo,exo\text{-}3,6\text{-}C_6Me_6H_2)]$ **2**. Conversely, the analogous reduction of the benzene complex **1a** results in the formation of a cyclohexa-1,3-diene complex $[Ru(\eta^6\text{-}C_{16}H_{16})(\eta^4\text{-}5,6\text{-}C_6H_8)]$ **3**. It has been proposed that in both instances 1,4-dienes are the products initially formed, but in the latter case the availability of *endo*-hydrogen atoms on the diene ring enables the complex to rearrange to form a more thermodynamically stable 1,3-diene product *via* a metal-hydride intermediate, Scheme 1(*a*).[19] Double nucleophilic additions at sites *para* to one another are consistent with charge control of the reaction but contrast markedly to double nucleophilic additions to the analogous bis(arene)iron compounds in which the products of reaction are a result of frontier orbital control, and result from 1,2-double addition.[1,2,22]

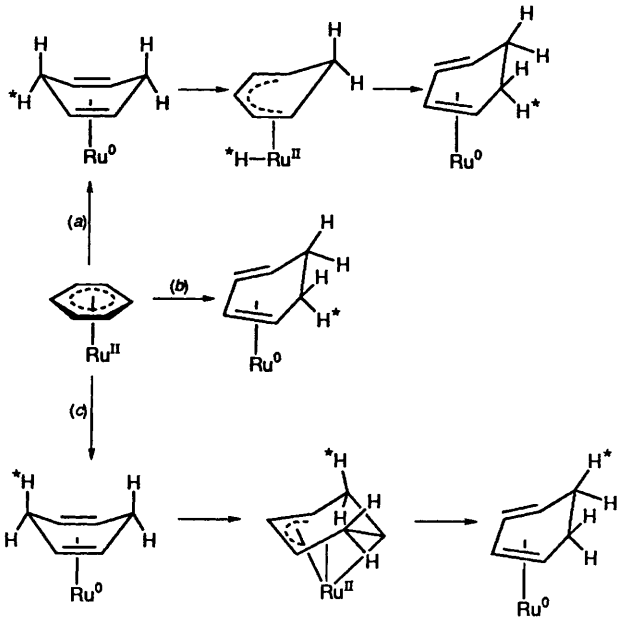


In our hands the reduction of **1e** with Red-Al gives rise to three isomeric products. The major component (67% of the isolated yield) was identified as **2** by its ^1H NMR spectrum, and results, as previously reported, from a 1,4-double addition of hydride to the hexamethylbenzene ring.[19] The two minor products were identified as (*i*) the 1,3-diene isomer of **2**, $[Ru(\eta^6\text{-}C_{16}H_{16})(\eta^4\text{-}exo,exo\text{-}5,6\text{-}C_6Me_6H_2)]$ **4** (8% of the isolated yield) and (*ii*) the *meta*-dihydro ruthenium(II) compound $[Ru(\eta^6\text{-}C_{16}H_{16})(1\text{-}\sigma\text{:}3\text{-}5\text{-}\eta\text{-}exo,exo\text{-}2,6\text{-}C_6Me_6H_2)]$ **5** (25%), (see below). Recrystallisation of this mixture gave only pure **2** as reported by Boekelheide and co-workers.[19]

Surprisingly, on carrying out the sodium borohydride reduction of **1e** we find that the 1,3-diene isomer **4** is formed as the sole product. Complex **4** (FAB mass spectrum *m/z* 474 based on ^{102}Ru) is readily identified by its ^1H NMR spectrum (Table 1) which exhibits a singlet resonance for the co-ordinated deck of the paracyclophane ligand at δ 4.09, a chemical shift characteristic of a neutral ruthenium(0) species (*cf.* complex **2**: δ 3.95). Three methyl resonances are observed and a quartet for the *exo*-hydrogen atoms [δ 1.74, 1.10 and 0.56 (d, ^3J = 6.8), CH_3; 1.18 (q, ^3J = 6.8 Hz, *exo*-H†]. In contrast, **2** displays only two methyl signals[19] and the resonance arising from the *exo*-hydrogen atoms [δ 1.27 (d, ^3J = 7.0) and 1.00 (s), CH_3; 3.41 (q, ^3J = 7.0 Hz), *exo*-H]. The infrared spectrum of **4** exhibits a strong band due to $\nu(CH_{exo})$ at 2808 cm^{-1}, shifting to

* Presence of water of crystallisation confirmed by the observation of ν(OH) in the infrared spectra of the complexes.

† Resonances assigned with the aid of homonuclear decoupling experiments where appropriate. ^1H NMR spectrum of **2** remeasured in $CDCl_3$ for comparative purposes.



Scheme 1 Mechanisms for the formation of cyclohexa-1,3-diene complexes (*a*) Metal–hydride mediated *endo* rearrangement of a cyclohexa-1,4-diene, (*b*) direct 1,2-double nucleophilic addition and (*c*) *exo*-sigmatropic shift of a cyclohexa-1,4-diene (starred hydrogen atoms are undergoing rearrangement)

2083 cm^{-1} in the dideuterio complex $[Ru(\eta^6\text{-}C_{16}H_{16})(\eta^4\text{-}exo,exo\text{-}5,6\text{-}C_6Me_6D_2)]$ **4'** confirming *exo* addition. The $\nu(CH_{exo})$ vibration in compound **2** occurs at 2751 cm^{-1}.

Complex **4** is structurally similar to the cyclohexa-1,3-diene compound **3**[19] and a wide range of (1,3-diene)iron(0) species formed by direct 1,2-double addition under conditions of frontier orbital control.[1,2,22] The question of whether **4** (and also **3**) is formed as a consequence of direct 1,2-double addition [Scheme 1 (*b*)] or results from a rearrangement of **2** (which might be the kinetic product) has important consequences for the validity of charge control models for nucleophilic additions to ruthenium. Unlike the case of **3**, complex **2** cannot isomerise to form **4** *via* an *endo*, metal-hydride mediated rearrangement pathway [Scheme 1(*a*)] because no *endo*-hydrogen atoms are available. Formation of **4** must therefore proceed *via* an *exo* pathway such as an intramolecular [1,3]- or series of [1,2]-sigmatropic shifts [Scheme 1(*c*)] or by direct 1,2-double addition [Scheme 1(*b*)].

The *meta*-dihydro complex **5** exhibits a singlet ^1H NMR resonance at δ 4.31 for the co-ordinated paracyclophane deck and, whilst this material could not be isolated in an isomerically pure form, the remainder of its ^1H NMR spectrum is consistent with the proposed ene-diyl formulation. Such a product could result either from a direct 1,3-double nucleophilic addition or possibly a [1,2]-H atom shift rearrangement of complex **2**. The complex exhibits four methyl resonances and a 2 H quartet resonance due to H_{exo} [δ 1.49 (s, 3 H), 1.46 (s, 6 H), 0.80 (d, 6 H, ^3J = 6.8) and 0.27 (s, 3 H), CH_3; 2.65 (q, ^3J = 6.8 Hz), *exo*-H]. The methyl resonance at δ 0.27 occurs at surprisingly high field and models show that the half-boat conformation of the proposed structure would bring the unique methyl substituent attached to the σ-co-ordinated site into close proximity to the metal centre. Such upfield shifts have also been noted in related ene-diyl compounds which are formed along with *ortho*-addition products on nucleophilic additions of H^- and CN^- to tri(carbonyl)(cyclohexadienyl)osmium(II) cations[23] and as the sole products of hydride addition to $[Mn(6\text{-}exo\text{-}PhC_6H_6)(NO)(L\text{–}L)]^+$ (L–L = $Ph_2PCH_2CH_2PPh_2$ or *cis*-$Ph_2PCH{=}CHPPh_2$).[24] The chemical shift of the protons of the co-ordinated deck of the paracyclophane ligand in **5** is at higher field than that observed for **2** and **4** consistent with a ruthenium(II) centre but lower than the values observed for cationic and dicationic ruthenium(II) complexes (δ 4.31, *cf. ca.* δ 5 and 6 respectively) suggesting a neutral compound. The chemical shift of H_{exo} is intermediate between that of **2** and **4** [δ 2.65, *cf.* 3.41 (**2**) and 1.18 (**4**)]. Hence it seems likely that **5** is a neutral ruthenium(II) compound.

In the synthesis of **4**, the relatively poor electrophilicity of complexed hexamethylbenzene coupled with the mild reducing nature of $Na[BH_4]$ has made it necessary for us to employ reaction times of *ca.* 72 h at room temperature in order to obtain good yields as opposed to *ca.* 2 h in the case of **2**. We considered the possibility that this longer reaction time might result in a slow rearrangement of **2** and **5** to form **4**. However, stirring of **1e** with excess Red-Al over a period of one week gives no change in the relative proportions of **2**, **4** and **5**. Isolation of **2** followed by stirring either alone, or in the presence of excess $Na[BH_4]$ in tetrahydrofuran (thf) for 7 d also does not result in isomerisation. Similarly, action of neither NaOH, $Na[BF_4]$, $B(OH)_3$, $BF_3{\cdot}Et_2O$, water nor heat (refluxing thf) results in conversion of **2** or **5** into **4**. This contrasts to the ene-diyl osmium compound $[Os(\eta^3\text{:}\sigma\text{-}C_6H_8)(CO_3)]$[23] which isomerises in refluxing hexane over a period of 5 h to the 1,3-diene analogue *via*. a proposed *endo* mechanism analogous to that suggested to be responsible for the formation of **3** [Scheme 1(*a*)]. In the case of **5** however, *endo* hydrogen atoms are absent.

We have noted that the formation of **4** is sensitive to aqueous quenching. If water is *not* added to destroy excess $Na[BH_4]$ during work-up, mixtures containing 20–40% **2** along with **4** (although no **5**) are formed instead of pure **4** in the case of the quenched reaction. Aqueous quenching is also a necessary feature of the Red-Al reduction of **1e** but does not result in the formation of a single isomer. In light of the fact that neither water, NaOH, $B(OH)_3$ nor water–$Na[BH_4]$–$Na[BF_4]$ mixtures bring about the conversion of **2** into **4** once it has been isolated we suggest that the effect of the water in the synthesis of **4** is simply to decompose or otherwise (for reasons of solubility) prevent the extraction of **2**, resulting solely in the isolation of **4**.

In general we conclude that the action of hydrides upon **1e** results in direct 1,2-, 1,3-and 1,4-double nucleophilic additions to form **4**, **5** and **2** respectively and that *no* rearrangement of **2** to form isomer **4** occurs. The ratio in which **2**, **4** and **5** are produced is determined primarily by the choice of reducing agent, thus the bulky Red-Al gives a second attack predominantly *para* to the more hindered sp^3 site[22] on the cyclohexadienyl ligand (formed after the first addition) resulting in formation of **2**. Use of the less sterically bulky reagent $Na[BH_4]$ results in a preponderance of 1,2-double addition to give **4** [Scheme 1(*b*)]. We have also examined the reduction of **1e** with $Na[AlH_2Et_2]$, a reagent structurally similar to Red-Al but with a slightly more bulky substituent directly adjacent to the aluminium (–CH_2– as opposed to –O–). This reagent also gives **2** as the major product (75%), along with **5** (25%) and essentially no **4**.

In an attempt to determine the viability of the *endo*-hydride transfer mechanism[19,23] we have examined the reaction of the benzene complex **1a** with sodium borodeuteride, $Na[BD_4]$. Reaction of **1a** with Red-Al gives the 1,3-diene complex **3**. If the formation of **3** occurs as a result of 1,4-double nucleophilic addition, followed by metal–hydride mediated rearrangement as previously suggested,[19] the product of the analogous $Na[BD_4]$ reduction would be a 1,3-diene exhibiting deuterons in the 2 and 5 positions [Fig. 1(*a*)], since the incoming nucleophile would finish in an olefinic site after rearrangement. Alternatively [Fig. 1(*b*)], direct 1,2-double nucleophilic addition would result in deuterons occupying the 5 and 6 positions.

In the case of **1a** the borohydride reduction proceeds much more efficiently than in that of **1e** as a consequence of the greater electrophilicity of the non-alkylated ring, and a good yield may be isolated after reaction times of *ca.* 4 h. Under these conditions the resulting yellow solid, $[Ru(\eta^6\text{-}C_{16}H_{16})(\eta^4\text{-}C_6H_6D_2)]$ **3'**, exhibits the expected ^1H NMR spectrum (C_6D_6) similar to that of **3** although the resonance due to the *exo* protons (δ 1.79) is greatly reduced in intensity. Similar results are obtained after

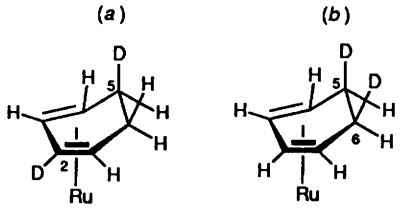


Fig. 1 Possible products arising from the action of $Na[BD_4]$ upon the benzene complex **1a**; (*a*) 1,4 addition followed by *endo* rearrangement and (*b*) 1,2 addition

7 d stirring of **3'** in the presence of $Na[BD_4]$ and no dependence upon aqueous quenching is observed. The incoroporation of deuterium solely into the *exo* aliphatic sites (consistent with direct 1,2-double addition) was confirmed by the ^2H NMR spectrum of the complex (Fig. 2) which exhibited a strong signal at δ 1.71 (*exo* CH_2) with very little evidence for deuterium incorporation at the olefinic sites δ 3.09 and 4.76. Similarly, the infrared spectrum of **3'** displays a single ν(CD) at 2112 cm^{-1} (shifted from 2824 cm^{-1} in **3**) consistent with *exo* co-ordination.

In an attempt to gain a greater understanding of the factors governing the regioselectivities and possible rearrangement pathways of these reactions we have examined the action of hydride upon related $[Ru(\eta^6\text{-}C_{16}H_{16})(\eta^6\text{-arene})][BF_4]_2$ compounds (arene = *p*-cymene **1b**, 1,2,4,5-tetramethylbenzene **1c** and pentamethylbenzene **1d**). In the case of **1d** (arene = pentamethylbenzene) we envisage the formation of up to three possible products, shown in Fig. 3. The 1,4-diene product [Fig. 3(*a*)] is unlikely given the possibility of an *endo*-hydride transfer rearrangement because the availability of an *endo*-hydrogen atom (assuming at least one nucleophilic addition takes place, as expected,[9] at the unmethylated site) should enable an *endo* rearrangement to a 1,3-diene, shown in Fig. 3(*b*), to take place. Formation of this 1,3-diene *via* the mechanism depicted in Scheme 1(*a*) would involve an intramolecular nucleophilic addition of hydride from the suggested M–H intermediate to one of the *methylated* sites of the intermediate cyclohexadienyl ring. Formation of the alternative 1,3-diene complex, Fig. 3(*c*), would occur by direct 1,2-double addition, Scheme 1(*b*).

These three possible isomers should be readily distinguishable from each other by their ^1H NMR spectra. The 1,4-diene complex, Fig. 3(*a*), is symmetrical and would therefore give rise to a singlet resonance for the prochiral protons of the cyclophane co-ordinated deck. The 1,3-diene species are both asymmetric and would cause a splitting of the co-ordinated ring resonance into an AA'BB' pattern as observed in other chiral [2.2]paracyclophane compounds.[18,25] In practice we find that the reaction of **1d** with *both* Red-Al and $Na[BH_4]$ gives a yellow solid $[Ru(\eta^6\text{-}C_{16}H_{16})(\eta^4\text{-}C_6Me_5H_3)]$ **6** displaying an AA'BB' quartet for the protons of the co-ordinated cyclophane ring in its ^1H NMR spectrum (δ 4.15, 4.11, ^3J = 5.9 Hz) clearly indicating a chiral 1,3-diene product. Interestingly however, no resonances are observed in the olefinic region of the spectrum which would correspond to the *endo*-rearranged product [Fig. 3(*b*)]. Also, a resonance observed at δ 0.44 (^2J = 13.1, ^3J = 3.3 Hz) assigned to the *endo*-hydrogen atom of the diene ring, is not a doublet as would be expected from the complex shown in Fig. 3(*b*). Instead this signal is a doublet of doublets displaying coupling constants typical of both geminal and vicinal coupling. The *endo*-hydrogen atom could only be coupled to *both exo* protons in this way if the complex possessed the structure shown in Fig. 3(*c*), *i.e.* the formation of **6** results from a direct 1,2-double addition in the same way as **4** in spite of the availability of an *endo*-hydrogen atom.

The ^1H NMR assignments for **6** were confirmed by preparation of the dideuteriated analogue, $[Ru(\eta^6\text{-}C_{16}H_{16})(\eta^4\text{-}C_6Me_5HD_2)]$ **6'** (by treatment of **1d** with $Na[BD_4]$). In the ^1H NMR spectrum of **6'** the resonances at δ 1.35 and 1.10, arising from the *exo* protons on the undeuteriated analogue were absent, while the resonance corresponding to H_{endo} (δ 0.44) occurred as a singlet, as did the resonance corresponding to the *endo*-methyl substituent, δ 0.66. The infrared spectrum of **6** displays $\nu(CH_{exo})$ at 2738 cm^{-1}. In **6'** this band shifted to 2093 cm^{-1} whilst the remainder of the region 2700–3100 cm^{-1} remained unchanged. Both **6** and **6'** displayed a band at 2925 cm^{-1} tentatively assigned to $\nu(CH_{endo})$.

Fig. 2 The ^2H NMR spectrum of $[Ru(\eta^6\text{-}C_{16}H_{16})(\eta^4\text{-}C_6H_6D_2)]$ **3'**

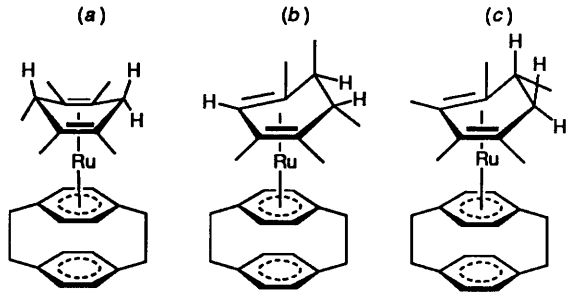


Fig. 3 Possible isomers of $[Ru(\eta^6\text{-}C_{16}H_{16})(\eta^4\text{-}C_6Me_5H_3)]$ **6**; (*a*) 1,4-double addition, (*b*) *endo* rearrangement and (*c*) 1,2-double addition or *exo* arrangement

Small quantities of a second product representing *ca.* 4% of the overall reaction yield in both the Red-Al and borohydride syntheses of **6** were also observed. This product was not isolated but, since it exhibits a singlet resonance for the cyclophane co-ordinated deck at δ 3.97 (*cf.* δ 3.95 for **2**) and a multiplet resonance at δ 3.46 assigned to the *exo*-hydrogen atoms from the incoming nucleophile (*cf.* **2** δ 3.41), we suggest it to be the 1,4-diene isomer of **6** shown in Fig. 3(*a*).

Action of $Na[BH_4]$ upon the 1,2,4,5-tetramethylbenzene complex **1c** in thf over a period of *ca.* 12 h again results in the formation of a (diene)ruthenium(0) complex $[Ru(\eta^6\text{-}C_{16}H_{16})(\eta^4\text{-}C_6Me_4H_4)]$ **7** (FAB mass spectrum *m/z* 446). According to arguments based on the accumulation of partial positive charges on the arene carbon atoms[2,9] initial nucleophilic additions should be more likely to occur *para* to one another to give a 1,4-diene product, since the two unmethylated sites should be the most electrophilic. In practice though, an asymmetric 1,3-diene product is obtained as is apparent from the large splitting of the ^1H NMR resonance arising from the protons of the co-ordinated cyclophane deck. The remainder of the spectrum bears a strong resemblance to that of **6** and selective homonuclear decoupling experiments along with analysis of coupling constants implies that, like **6**, **7** possesses an *endo*-methyl group attached to an aliphatic ring site and therefore also results from 1,2-double addition and not an *endo*-hydride transfer. Also in common with **6**, a small quantity (*ca.* 2%) of a symmetric (cyclophane)ruthenium(0) species is observed in the crude reaction product (co-ordinated cyclophane ring δ 3.96, singlet) suggestive of the presence of a small quantity of the 1,4-diene isomer of **7**.

Reduction of the *p*-cymene complex **1b** with Red-Al and $Na[BH_4]$ (in the absence of aqueous quenching) also results in the formation of a chiral 1,3-diene complex of formula $[Ru(\eta^6\text{-}C_{16}H_{16})\{\eta^4\text{-}1\text{-}(CHMe_2)\text{-}4\text{-}MeC_6H_6\}]$ **8a**, as would be expected from the product of a direct 1,2-double hydride addition at the least alkylated sites. The methyl and isopropyl substituents occupy the two terminal olefinic sites, C(4) and C(1), whilst the two olefinic hydrogen atoms occur as an AB quartet in the ^1H NMR spectrum, δ 4.21 and 4.07 ($^3J_{HH}$ = 3.4 Hz consistent with the *cis* geometry). Surprisingly, if the reduction is carried out with $Na[BH_4]$ and water added to the reaction mixture a

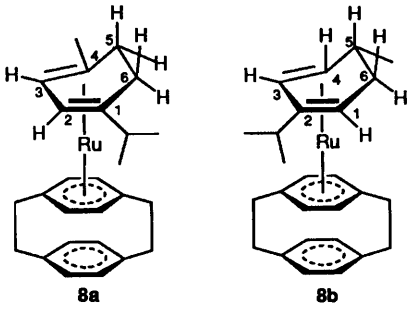
Table 1 Proton NMR data for new compounds[a]

	Compound	δ		
		Cyclophane ring	Cyclophane bridge	Ligand
2	$[Ru(\eta^6\text{-}C_{16}H_{16})(\eta^4\text{-}3,6\text{-}C_6Me_6H_2)]$[b]	6.65 (s, 4 H), 3.95 (s, 4 H)	3.04, 2.69 (AA′XX′, 8 H)	3.41 (q, 2 H, ^3J = 7.0, *exo*-H), 1.27 (d, 6 H, ^3J = 7.0, CH_3), 1.00 (s, 12 H, CH_3)
2′	$[Ru(\eta^6\text{-}C_{16}H_{16})(\eta^6\text{-}3,6\text{-}C_6Me_6D_2)]$	6.65 (s, 4 H), 3.95 (4 H)	3.04, 2.69 (AA′XX′, 8 H)	1.27 (s, 6 H, CH_3), 1.00 (s, 12 H, CH_3)
4	$[Ru(\eta^6\text{-}C_{16}H_{16})(\eta^4\text{-}5,6\text{-}C_6Me_6H_2)]$	6.63 (s, 4 H), 4.09 (s, 4 H)	3.04, 2.67 (AA′XX′, 8 H)	1.74 (s, 6 H, CH_3), 1.18 (q, 2 H, ^3J = 6.8, *exo*-H), 1.10 (s, 6 H, CH_3), 0.56 (d, 6 H, ^3J = 6.8, CH_3)
4′	$[Ru(\eta^6\text{-}C_{16}H_{16})(\eta^6\text{-}5,6\text{-}C_6Me_6D_2)]$	6.64 (s, 4 H), 4.10 (s, 4 H)	3.04, 2.67 (AA′XX′, 8 H)	1.74 (s, 6 H, CH_3), 1.10 (s, 6 H, CH_3), 0.56 (s, 6 H, CH_3)
5	$[Ru(\eta^6\text{-}C_{16}H_{16})(\sigma{:}\eta^3\text{-}C_6Me_6H_2)]$	6.71 (s, 4 H), 4.31 (s, 4 H)	3.04, 2.56 (AA′XX′, 8 H)	2.65 (q, 2 H, ^3J = 6.8, *exo*-H), 1.49 (s, 3 H, CH_3), 1.46 (s, 6 H, CH_3), 0.80 (d, 6 H, ^3J = 6.8, CH_3), 0.27 (s, 3 H, CH_3)
6	$[Ru(\eta^6\text{-}C_{16}H_{16})(\eta^4\text{-}C_6Me_5H_3)]$	6.66 (s, 4 H), 4.15, 4.11 (AA′BB′, 4 H, ^3J = 5.9)	3.06, 2.68 (AA′XX′, 8 H)	1.75 (s, 3 H, CH_3), 1.74 (s, 3 H, CH_3), 1.35 (dd, 1 H, ^2J = 13.1, ^3J = 5.8, *exo*-H^5), 1.26 (s, 3 H, CH_3), 1.16 (s, 3 H, CH_3), 1.10 (m, 1 H, *exo*-H^6), 0.66 (d, 3 H, ^3J = 6.4, CH_3), 0.44 (dd, 1 H, ^2J = 13.1, ^3J = 3.3, *endo*-H^5)
6′	$[Ru(\eta^6\text{-}C_{16}H_{16})(\eta^4\text{-}C_6Me_5HD_2)]$	6.66 (s, 4 H), 4.15, 4.11 (AA′BB′, 4 H, ^3J = 5.9)	3.06, 2.68 (AA′XX′, 8 H)	1.76 (s, 3 H, CH_3), 1.75 (s, 3 H, CH_3), 1.26 (s, 3 H, CH_3), 1.17 (s, 3 H, CH_3), 0.66 (s, 3 H, CH_3), 0.43 (s, 1 H, *endo*-H^5[c])
7	$[Ru(\eta^6\text{-}C_{16}H_{16})(\eta^4\text{-}C_6Me_4H_4)]$	6.68 (s, 4 H), 4.33, 4.04 (AA′BB′, 4 H, ^3J = 5.8)	3.10, 2.74 (AA′XX′, 8 H)	4.11 (s, 1 H, H^2), 1.68 (s, 3 H, CH_3), 1.40 (dd, 1 H, ^2J = 13.2, ^3J = 7.6, *exo*-H^5), 1.25 (s, 3 H, CH_3), 1.15 (qdd, 1 H, ^3J = 7.6, 6.6, 3.0, *exo*-H^6), 1.05 (s, 3 H, CH_3), 0.64 (d, 3 H, ^3J = 6.6, CH_3), 0.46 (dd, 1 H, ^2J = 13.2, ^3J = 3.0, *endo*-H^5)
8a	$[Ru(\eta^6\text{-}C_{16}H_{16})\{\eta^4\text{-}1\text{-}(CHMe_2)\text{-}4\text{-}MeC_6H_6\}]$	6.70 (s, 4 H), 4.37, 4.16 (AA′BB′, 4 H, ^3J = 5.8)	3.09, 2.78 (AA′XX′, 8 H)	4.21, 4.07 (AB, 2 H, ^3J = 3.4, H^2, H^3), 1.42–1.15 (m, 4 H, H^5, H^6), 1.32 (spt, 1 H, ^3J = 6.8, C*H*Me_2), 1.22 (s, 3 H, CH_3), 0.92 (d, 3 H, ^3J = 6.8, CH*Me*$_2$), 0.89 (d, 3 H, ^3J = 6.8, CH*Me*$_2$)
8b	$[Ru(\eta^6\text{-}C_{16}H_{16})\{\eta^4\text{-}2\text{-}(CHMe_2)\text{-}5\text{-}MeC_6H_6\}]$	6.71, 6.70 (AA′BB′, 4 H, ^3J = 3.3) 4.47, 4.22 (AA′BB′, 4 H, ^3J = 5.8)	3.09, 2.78 (AA′XX′, 8 H)	4.24 (d, 1 H, ^3J = 5.6, H^3), 2.49 (m, 2 H, H^1, H^4), 1.89 (spt, 1 H, ^3J = 6.8, C*H*Me_2), 1.63 (m, 1 H, *exo*-H^5), 1.53 (ddd, 1 H, ^2J = 12.8, ^3J = 4.2, 10.7, *exo*-H^6), 0.94 (d, 3 H, ^3J = 6.8, CH*Me*$_2$), 0.90 (d, 3 H, ^3J = 6.8, CH*Me*$_2$), 0.76 (ddd, 1 H, ^2J = 12.8, ^3J = 1.7, 4.2, *endo*-H^6), 0.72 (d, 3 H, ^3J = 6.7, CH_3)
9	$[Ru(\eta^6\text{-}C_{16}H_{16})(\eta^5\text{-}C_6Me_7)][BF_4]$	6.80 (s, 4 H), 5.03 (s, 4 H)	3.22, 2.86 (AA′XX′, 8 H)	2.28 (s, 3 H, CH_3), 1.86 (s, 6 H, CH_3), 1.39 (s, 6 H, CH_3), 1.04 (s, 3 H, *endo*-CH_3), 0.15 (s, 3 H, *exo*-CH_3)

Table 1 (*continued*)

10	$[Ru(\eta^6\text{-}C_{16}H_{16})(\eta^5\text{-}C_6H_6Me)][BF_4]$	6.85 (s, 4 H), 5.36 (s, 4 H)	3.26, 3.02 (AA′XX′, 8 H)	6.14 (t, 1 H, ^3J = 5.1, *para*-H), 4.79 (t, 2 H, ^3J = 5.5, *meta*-H), 3.61 (t, 2 H, ^3J = 6.7, *ortho*-H), 2.23 (m, 1 H, *endo*-H), 0.30 (d, 3 H, ^3J = 6.6, CH_3)
11	$[Ru(\eta^6\text{-}C_{16}H_{16})(\eta^5\text{-}C_6H_6OMe)][BF_4]$ [d]	6.92 (s, 4 H), 5.50 (s, 4 H)	3.31, 3.06 (AA′XX′, 8 H)	6.01 (t, 1 H, ^3J = 5.2, *para*-H), 4.99 (t, 2 H, ^3J = 6.0, *meta*-H), 4.04 (t, 2 H, ^3J = 6.8), 3.38 (t, 1 H, ^3J = 5.9, *endo*-H), 2.88 (s, 3 H, OMe)
12	$[Ru(\eta^6\text{-}C_{16}H_{16})\{\eta^5\text{-}C_6Me_5(CH_2)\}][BF_4]$	6.84 (s, 4 H), 5.10 (s, 4 H)	3.24, 2.88 (AA′XX′, 8 H)	3.72 (s, 2 H, $=CH_2$), 2.23 (s, 3 H, CH_3), 1.99 (s, 6 H, CH_3), 1.76 (s, 6 H, CH_3)
13	$[Ru(\eta^6\text{-}C_{16}H_{16})\{\eta^4\text{-}C_6Me_4(CH_2)_2\}]$	6.65 (s, 4 H), 4.23 (s, 4 H)	3.08, 2.71 (AA′XX′, 8 H)	4.64 (s, 2 H, $=CH_2$), 4.20 (s, 2 H, $=CH_2$), 1.85 (s, 6 H, CH_3), 1.54 (s, 6 H, CH_3)
16	$[Ru(\eta^6\text{-}C_{16}H_{16})(\eta^3\text{-}C_6Me_6H_3)][BF_4]$	6.85 (s, 4 H), 4.80 (s, 4 H)	3.24, 2.98 (AA′XX′, 8 H)	1.95 (s, 6 H, CH_3), 1.38 (d, 6 H, ^3J = 2.5 av., *exo*-CH_3), 1.22 (d of q, 2 H, ^3J = 6.6, 4.1 av., H_{exo}), 0.72 (d, 6 H, ^3J = 6.6, *endo*-CH_3), −10.80 (t of spt, 1 H, ^3J = 4.1, 2.5 av.)
16′	$[Ru(\eta^6\text{-}C_{16}H_{16})(\eta^3\text{-}exo\text{-}C_6Me_6HD_2)][BF_4]$	6.86 (s, 4 H), 4.80 (s, 4 H)	3.22, 2.96 (AA′XX′, 8 H)	1.93 (s, 6 H, CH_3), 1.36 (d, 6 H, ^3J = 2.3 av., *exo*-CH_3), 0.68 (s, 6 H, *endo*-CH_3), −10.91 (spt, 1 H, ^3J = 2.3 av.)
16″	$[Ru(\eta^6\text{-}C_{16}H_{16})(\eta^3\text{-}endo\text{-}C_6Me_6H_2D)][BF_4]$	6.86 (s, 4 H), 4.80 (s, 4 H)	3.23, 2.97 (AA′XX′, 8 H)	1.93 (s, 6 H, CH_3), 1.36 (s, 6 H, *exo*-CH_3), 1.22 (q, 2 H, ^3J = 6.2, H_{exo}), 0.70 (d, 6 H, ^3J = 6.2, *endo*-CH_3)
17	$[Ru(\eta^6\text{-}C_{16}H_{16})(\eta^3\text{-}endo\text{-}C_6Me_6H_2D)][H(CF_3CO_2)_2]$	6.79 (s, 4 H), 4.72 (s, 4 H)	3.22, 2.95 (AA′XX′, 8 H)	8.80 [s, br, 1 H, $H(CF_3CO_2)_2$], 1.91 (s, 6 H, CH_3), 1.34 (s, 6 H, *exo*-CH_3), 1.18 (q, 2 H, ^3J = 6.0, *exo*-H), 0.69 (d, 6 H, ^3J = 6.0 av., *endo*-CH_3)
18	$[Ru(\eta^6\text{-}C_{16}H_{16})\{\eta^3\text{-}(HCH_2)(CH_2)C_6Me_4H_4\}][BF_4]$	6.88 (s, 4 H), 5.03 (s, 4 H)	3.25, 3.10 (AA′XX′, 8 H)	2.08 (d of q, 2 H, ^3J = 4.9, 6.8, H_d, $H_{d'}$), 1.43 (d of q, 2 H, ^3J = 4.9, 6.6, H_e, $H_{e'}$), 0.95 (d, 6 H, ^3J = 6.6, Me_e, $Me_{e'}$), 0.82 (d, 6 H, ^3J = 6.8, Me_d, $Me_{d'}$), −1.52 (s, br, 5 H, $H_{a,b,c}$, $H_{b,c'}$)
19	$[Ru(\eta^6\text{-}C_{16}H_{16})\{\eta^4\text{-}(CH_2)_2C_6Me_4H_4\}]$	6.70 (s, 4 H), 4.46 (s, 4 H)	3.11, 2.80 (AA′XX′, 8 H)	1.92 (d of q, 2 H, ^3J = 4.9, 6.7, *exo*-H), 1.45 (s, 2 H, H_{anti}), 1.19 (d of q, 2 H, ^3J = 4.9, 6.7, *endo*-H), 0.86 (d, 6 H, ^3J = 6.7, *exo*-CH_3), 0.60 (d, 6 H, ^3J = 6.7, *endo*-CH_3), −0.71 (s, 2 H, H_{syn})
20	$[Ru(\eta^6\text{-}C_{16}H_{16})(\eta^3\text{-}C_6Me_5H_4)][BF_4]$	6.86 (s, 4 H), 4.88, 4.83 (AA′BB′, 4 H, ^3J = 6.6)	3.23, 2.97 (AA′XX′, 8 H)	1.86 (s, 3 H, CH_3), 1.77 (s, 3 H, CH_3), 1.75 (s, 3 H, CH_3), 1.73 (m, 1 H, *exo*-H), 1.05 (d, 3 H, ^3J = 4.8 av., *exo*-CH_3), 0.91 (m, 1 H, *exo*-H), 0.75 (d, 3 H, 6.7, *endo*-CH_3), −4.56 (s, br, 1 H, *endo*-H), −5.25 (s, br, 1 H, *endo*-H)
21	$[Ru(\eta^6\text{-}C_{16}H_{16})(\eta^3\text{-}C_6Me_4H_5)][BF_4]$	6.86 (s, 4 H), 4.94, 4.80 (AA′BB′, 4 H, ^3J = 6.3)	3.23, 3.03 (AA′XX′, 8 H)	3.60 (dd, 1 H, J = 3.7, 1.8, $H_{c'}$), 2.12 (dd, 1 H, J = 14.0, 2.1 av., *exo*-$H_{a'}$), 1.89 (s, 3 H, CH_3), 1.86 (s, 3 H, CH_3), 0.91 (d, 3 H, ^3J = 5.8 av., *exo*-CH_3), 0.75 (m, 1 H, *exo*-$H_{a'}$), 0.70 (d, 3 H, ^3J = 6.4, *endo*-CH_3), −1.88 (s, br, 1 H, *endo*-$H_{b'}$), −7.68 (s, br, 1 H, *endo*-H_a)

[a] Solvent $CDCl_3$ unless otherwise stated, 400 MHz, 298 K, J_{HH} in Hz, δ in ppm, s = singlet, d = doublet, t = triplet, q = quartet, spt = septet, m = multiplet, dd = doublet of doublets, dt = doublet of triplets, ddd = doublet of doublets of doublets, br = broad. [b] Previously synthesised by Boekelheide and co-workers.[19] [c] Deuterium coupling not resolved. [d] Solvent CD_3NO_2.



different isomer is obtained, $[Ru(\eta^6\text{-}C_{16}H_{16})\{\eta^4\text{-}2\text{-}(CHMe_2)\text{-}5\text{-}MeC_6H_6\}]$ **8b**. Complex **8b** is characterised by the observation of a single internal olefinic doublet (δ 4.24) in place of the AB quartet observed for **8a** and the appearance of a multiplet corresponding to the terminal olefinic hydrogen atoms on C(1) and C(4) (δ 2.49, 2 H). Strong evidence for the aliphatic nature of the methyl substituent on C(5) is the doublet resonance at δ 0.72 (^3J = 6.7 Hz, 3 H). In **8a** the methyl substituent is attached to the terminal olefinic site C(4) and occurs as a singlet (δ 1.22). The assignment of the ^{1}H NMR spectrum of **8b** was confirmed by an extensive series of homonuclear decoupling experiments which, in conjunction with analysis of coupling constant data, suggested that the methyl substituent on C(5) adopts an *endo* stereochemistry. This would imply that **8b** could result from a net *exo* [1,3] H-shift of **8a**, but not an *endo* metal–hydride mediated rearrangement. The relationship between **8a** and **8b** is thus similar to that between **2** and **4**.

The observation of 1,2-double additions in complexes **1a**–**1e** is consistent with the chemistry of related bis(arene)iron dications, where deuteriation studies and reactions with nucleophiles other than hydride have also shown that double nucleophilic additions occur in a 1,2-fashion and thus the thermodynamic and kinetic products are one and the same.[2,22] Extended Hückel calculations on the cation $[Fe(\eta^6\text{-}C_6H_6)(\eta^5\text{-}C_6H_7)]^+$ have demonstrated that the greatest partial positive charges reside on the η^6-benzene ring (+0.04 to +0.08) and thus, under charge controlled conditions a second nucleophilic addition should give a bis(cyclohexadienyl)iron(II) complex, as frequently observed in non-cyclophane ruthenium compounds.[5] Within the cyclohexadienyl ring itself the greatest partial positive charges reside upon the carbon atoms *meta* (+0.06) and *para* (+0.05) to the saturated site (Fig. 4) and so 1,4- or 1,3-double additions would be expected (as observed in the Red-Al reduction of **1e**). The charge at the site *ortho* to the sp^3 carbon atoms has a small net negative charge (−0.01). Hence it has been concluded that in the case of the iron complexes, nucleophilic additions do not occur under charge control and a frontier-molecular-orbital model for the reaction is more satisfactory.[2,22]

Clearly a fine balance exists between the factors affecting regioselectivity in double nucleophilic addition reactions. The observation of 1,3- and 1,4-additions at a given ring, when Red-Al is used as the reducing agent, could be a result of both the steric bulk of the reagent and its strongly reducing nature, resulting in a change from orbital to charge controlled reactivity. Use of the inert spectator ligand [2.2]paracyclophane has enabled us to show that for practical purposes products of 1,2-double additions at a given ring are the norm in the case of ruthenium as well as the iron and osmium[23] analogues and hence occur under frontier-orbital control. However it should be noted that the use of water in the 'work-up' has a significant impact on the identity of the *isolated* product.

Synthesis of Functionalised Diene Complexes.—Direct interaction of complexes of type **1** with nucleophiles other than hydride in dry thf proved to be inefficient in generating

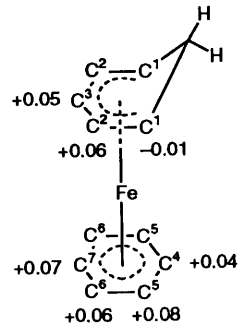


Fig. 4 Total calculated charges on carbon atoms in the cation $[Fe(\eta^6\text{-}C_6H_6)(\eta^5\text{-}C_6H_7)]^+$ (taken from ref. 22)

difunctionalised (diene)ruthenium(0) complexes. It was found that LiMe was insufficiently nucleophilic to effect a second addition to the hexamethylbenzene complex **1e** and only the heptamethyl cyclohexadienyl compound $[Ru(\eta^6\text{-}C_{16}H_{16})(\eta^5\text{-}C_6Me_7)][BF_4]$ **9** (FAB mass spectrum *m/z* 487, M^+) was isolated [characterised by ^{1}H NMR spectroscopy: five methyl signals, δ 2.28 (3 H), 1.86 (6 H), 1.39 (6 H), 1.04 (3 H) and 0.15 (3 H)]. Action of a 1 mole equivalent of LiMe upon the more electrophilic benzene complex **1a** also gave rise to a mono-methyl compound $[Ru(\eta^6\text{-}C_{16}H_{16})(\eta^5\text{-}C_6H_6Me)][BF_4]$ **10**, analogous to **9** [added methyl group δ 0.30 (d, ^3J = 6.6 Hz)] although the reaction was not clean. Addition of excess LiMe, however, and extraction into hexane gave rise to an air-sensitive yellow oil which was shown by ^{1}H NMR spectroscopy to consist of at least two major species. Two co-ordinated cyclophane ring resonances were observed [δ 3.96 (s) and 4.07 (AA'BB' q)] whilst the remainder of the spectrum was consistent with a mixture of isomers of formula $[Ru(\eta^6\text{-}C_{16}H_{16})(\eta^4\text{-}C_6H_6Me_2)]$. Pure samples of these materials could not be isolated.

Interaction of **1a** with LiMe in methanol provides a convenient high yield synthesis of the methoxy complex $[Ru(\eta^6\text{-}C_{16}H_{16})(\eta^5\text{-}C_6H_6OMe)][BF_4]$ **11**. The analogous treatment of **1e** with a base (LiMe, LiBu^n or KOH) in methanol however, results in the formation of the deprotonation product $[Ru(\eta^6\text{-}C_{16}H_{16})\{\eta^5\text{-}C_6Me_5(CH_2)\}][BF_4]$ **12**. This material was previously synthesised by us[18] from the action of KOH upon **1e** and incorrectly identified as the hydroxide addition product $[Ru(\eta^6\text{-}C_{16}H_{16})(\eta^5\text{-}C_6Me_6OH)][BF_4]$. Re-examination of our data reveals this product is closely similar to $[Ru(\eta^6\text{-}C_6Me_6)\{\eta^5\text{-}C_6Me_5(CH_2)\}]^+$, the product of the deprotonation of bis(hexamethylbenzene)ruthenium(II), reported by Gladfelter *et al.*[26,27] Both complexes display singlet resonances at δ 3.5–3.8 due to the methylene protons while the infrared spectrum of **12** displays a band corresponding to the unco-ordinated double bond at 1592 cm^{-1}. Complex **12** has also now been synthesised by action of 1 mole of KOBu^t upon **1e** in dry thf precluding the possibility of the formation of a hydroxide containing product.

Formation of complexes such as **12** result from the enhanced acidity of benzylic hydrogen atoms (*e.g.* on methyl substituents) of co-ordinated arenes and is a well documented phenomenon.[1,26–28] In the case of bis(arene) metal cations it has been demonstrated that either one or two protons (from substituents *ortho* to one another) may be abstracted, to generate respectively cyclohexadienyl complexes with one exocyclic double bond, such as **12**, or *o*-xylylene species in which the reduced metal centre is bound to the endocyclic double bonds.[26–28] In contrast to these results however, Bennett *et al.*[29] have recently demonstrated that double deprotonation of the (hexamethylbenzene)ruthenium(II) phosphine complexes $[Ru(\eta^6\text{-}C_6Me_6)(ONO_2)(PR_3)_2][NO_3]$ [PR_3 = PMe_2Ph, $PMePh_2$ or $P(OMe)_3$] in the presence of phosphine generates the (*o*-xylylene)ruthenium(0) compounds $[Ru\{\eta^4\text{-}C_6Me_4(CH_2)_2\}(PR_3)_3]$, in which the metal atom is bound to the exocyclic double bonds.

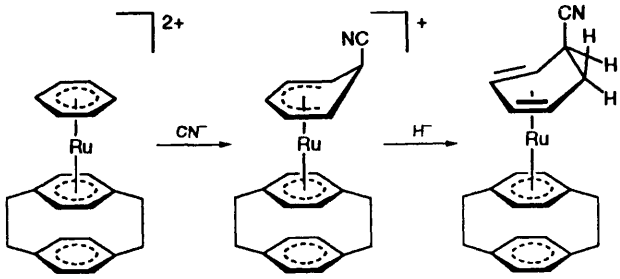
We find that reaction of the hexamethylbenzene complex **1e** with 2 equivalents of KOBu^t results in the double

deprotonation of the hexamethylbenzene ligand to give the mildly air-sensitive tetramethyl *o*-xylylene complex $[Ru(\eta^6\text{-}C_{16}H_{16})\{\eta^4\text{-}C_6Me_4(CH_2)_2\}]$ **13** (FAB mass spectrum *m/z* 470) with no trace of deprotonation of the cyclophane ligand observed. Complex **13** exhibits two resonances for the terminal olefinic protons, δ 4.64 and 4.20, characteristic of binding of the ligand through the endocyclic double bonds.[26,27] In contrast exocyclic complexes exhibit resonances due to H_{anti} and H_{syn} at much higher field, *e.g.* $[Ru\{\eta^4\text{-}C_6Me_4(CH_2)_2\}\{P(OMe)_3\}_3]$, δ 2.54 and 0.23.[29] The singlet resonance for the co-ordinated cyclophane deck is observed at δ 4.23, consistent with a neutral ruthenium(0) complex whilst the infrared spectrum of **13** exhibits a band of medium intensity at 1590 cm^{-1} (*cf. ca.* 1600 cm^{-1} for $[Mn\{C_6Me_4(CH_2)_2\}(CO)_3]^+$ [28]) assigned to the *exo*-methylene C=C bonds.

The synthesis of **13** is reversible and addition of HBF_4 (40% aq.) to a hexane solution of **13** regenerates **1e**. Careful addition of $HBF_4 \cdot Et_2O$ to an ether solution of **13** at low temperature also results in the reformation of **1e** along with a little **12**.

In view of the problems encountered in carrying out direct double addition of nucleophiles other than hydride we turned our attention to the generation of monofunctionalised diene species *via* a stepwise strategy (Scheme 2) involving $Na[BH_4]$ reduction of functionalised cyclohexadienyl complexes such as $[Ru(\eta^6\text{-}C_{16}H_{16})(\eta^5\text{-}C_6Me_6CN)][BF_4]$ **14**, which we have previously shown may readily be generated in good yields.[18] Reduction of the cyano complex **14** with $Na[BH_4]$ proceeds slowly at room temperature over a period of days to generate small quantities (*ca.* 20% of the isolated product) of the functionalised 1,3-diene complex $[Ru(\eta^6\text{-}C_{16}H_{16})\{\eta^4\text{-}C_6Me_6H(CN)\}]$ **15** as well as large quantities of **4** as a contaminant. The formation of **4** must result from loss of cyanide, which is clearly a better leaving group than hydride. Because **15** was only obtained in low yield and was relatively air sensitive it was not isolated. Its existence was however, confirmed by its ^1H NMR spectrum which exhibits an AA'BB' pattern for the co-ordinated ring protons of the cyclophane ligand (δ 4.28 and 4.17, ^3J = 6.6 Hz) indicating that the complex is chiral and thus possesses a 1,3-diene structure analogous to **4**.

Protonation of Ruthenium(0) *Complexes*.—Reaction of the electron-rich ruthenium(0) 1,3-diene complex **4** with HBF_4 (40% aq.) with vigorous stirring in hexane results in the formation of a pale yellow, air- and moisture-stable precipitate of $[Ru(\eta^6\text{-}C_{16}H_{16})(C_6Me_6H_3)][BF_4]$ **16**. Analytical data indicated the presence of one mole of water and this was confirmed by the observation of ν(OH) in the infrared spectrum of the complex. The FAB mass spectrum of the material displays only a single peak *m/z* 475 (with the expected isotope distribution characteristic of ruthenium) as expected for the cation in **16**, with no trace of fragmentation peaks of measurable intensity, implying that the water is not strongly associated with the complex. Retention of water was found to be common to a number of $[BF_4]$ salts of similar species (see below) and the related protonolysis product $[Ru\{\eta^3\text{-}(HCH_2)(CH_2)C_6H_4)\}(PMe_2Ph)_3][PF_6]$ also exists as a hydrate.[29] The presence of the $[BF_4]$ anion was confirmed by the observation of ν(BF) in the infrared spectrum. The room-temperature ^1H NMR spectrum of **16** exhibits three resonances of equal intensity arising from the methyl substituents of the $C_6Me_6H_3$ ring. A further aliphatic resonance was assigned to H_{exo} and a high field 'hydridic' signal was also observed [δ 1.95 (s), 1.38 (d, J_{obs} = 2.5) and 0.72 (d, J_{obs} = 6.6), CH_3; 1.22 (d of q, J_{obs} = 6.6, 4.1), *exo*-H; −10.80 (t of spt, J_{obs} = 4.1, 2.5 Hz)]. The peak due to the co-ordinated deck of the [2.2]paracyclophane ligand occurred as a singlet (implying an apparent plane of symmetry in the $C_6Me_6H_3$ ligand) at δ 4.80. This is at the lower field end of the chemical shift range expected for a monocationic ruthenium(II) species.[25] The symmetrical nature of the spectrum apparently implies that **16** exists as a metal hydride in its ground state, and contains an $\eta^4\text{-}C_6Me_6H_2$ 1,3-diene ligand, consistent with protonation and oxidation of the metal centre {*cf.* oxidation of the ruthenium(0) bis(phosphine) compounds $[Ru(\eta^6\text{-}C_6Me_6)(PR_3)_2]$ (R = Me or OMe) with $[NH_4][PF_6]$ to give the ruthenium(II) hydrido complexes $[Ru(\eta^6\text{-}C_6Me_6)(PR_3)_2H][PF_6]$}.[30–32] However, a series of homonuclear decoupling experiments revealed significant coupling of the hydridic resonance with (*i*) the *exo* ring protons (δ 1.22, 4.1 Hz) and (*ii*) the methyl signal at δ 1.38, 2.5 Hz, possibly implying an agostic[33] interaction.



Scheme 2 Stepwise strategy for the generation of functionalised (diene)ruthenium(0) species

The room-temperature ^1H-coupled ^{13}C spectrum of **16** (Fig. 5) is also relatively simple, displaying three resonances for the C_6 ring carbon atoms [δ 91.51 (s, C_c and $C_{c'}$), 59.25 (d, J_{obs} = 36.0, C_b and $C_{b'}$) and 38.45 (d, J_{obs} = 129.8, C_a and $C_{a'}$)]. The observed $^1J_{CH}$ on the resonance at δ 38.45 is typical of an sp^3 aliphatic coupling[34] and this resonance is assigned to the saturated carbon atoms C_a and $C_{a'}$. The resonance at δ 59.25 is assigned to $C_b/C_{b'}$ on the basis of a selective heteronuclear decoupling experiment: continuous irradiation of the ^1H signal at δ −10.80 resulted in the collapse of the 36 Hz doublet at δ 59.25 into a singlet resonance, in the ^1H-coupled ^{13}C spectrum, displaying a strong nuclear Overhauser effect (NOE) enhancement in intensity with respect to the remainder of the peaks in the spectrum, indicating that the hydridic proton does indeed form part of an agostic CH bond. The observed coupling of 36.0 Hz is too large for the formulation of **16** as a full hydride (it is estimated that hydridic couplings generally fall in the region 0–10 Hz[33]) but is also atypical of an agostic CH bond for which a value of 60–100 Hz would be expected.[33,35] The fluxional bis(ethylene)cobalt(III) complex $[Co(C_5Me_5)(\eta\text{-}C_2H_4)_2H]^+$ [33] however, exhibits a very similar low $^1J_{CH}$ coupling constant (33.5 Hz) as a result of the dynamic averaging of two degenerate agostic modes. This small coupling of 36.0 Hz is thus rationalised as a dynamic average (Scheme 3) of the two static couplings of the agostic proton with C_b and $C_{b'}$, *i.e.* in a slow exchange regime $^1J_{C_bH} \approx 72$ and $^1J_{C_{b'}H} \approx 0$ Hz.

Attempts were made to freeze out this rapid exchange by low-temperature ^1H NMR spectroscopy but the spectrum remained relatively unchanged in the temperature range +50 to −90 °C although at the latter temperature considerable broadening of a number of resonances had occurred. This was most noticeable on the signal due to the co-ordinated deck of the [2.2]-paracyclophane ligand. In the static complex this resonance would be expected to exhibit an AA'BB' pattern (or eight line signal if rotation about the ruthenium–cyclophane bond is slow) as a consequence of the loss of the dynamic plane of symmetry in the agostic ligand. Rapid exchange is not unexpected for systems of this kind and has previously been observed in related compounds.[36] Use of a mixed CD_2Cl_2–CHF_2Cl solvent allowed examination of the spectrum down to −135 °C, Fig. 6 (the more convenient CD_2Cl_2–CF_2Cl_2 mixture was unsuitable because of the low solubility of the complex in this medium). Between −90 °C and −110 °C the resonances due to H_{exo} and those arising from the methyl groups attached to the olefinic sites $C_b/C_{b'}$ and $C_c/C_{c'}$ (δ 1.95 and 1.38) broadened markedly, whilst the *endo*-methyl substituent (δ 0.72) remained relatively unaffected. At −110 °C the resonance due to the co-

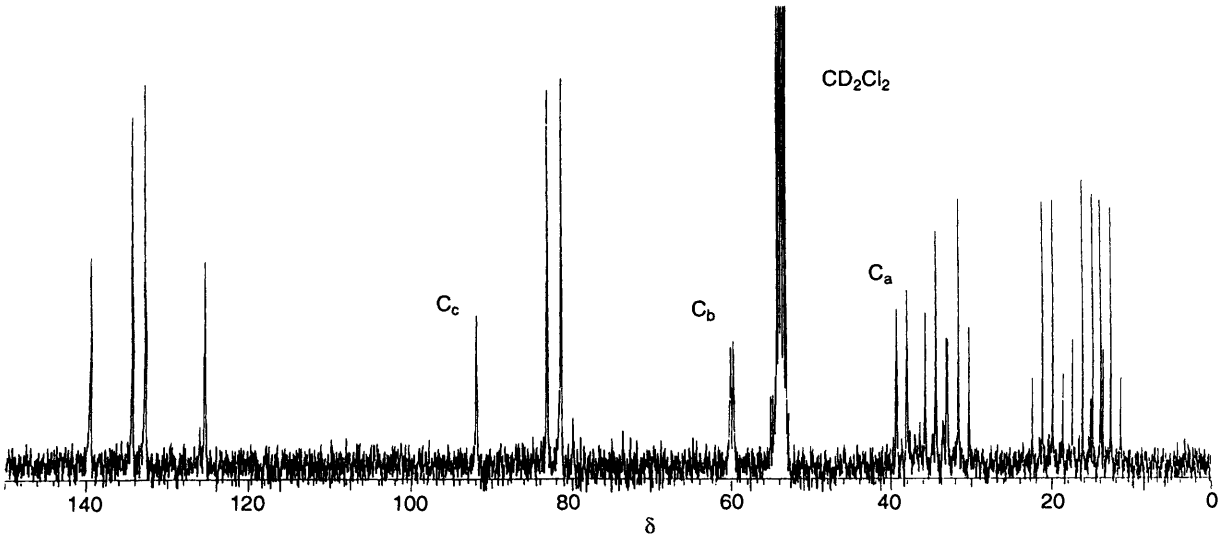
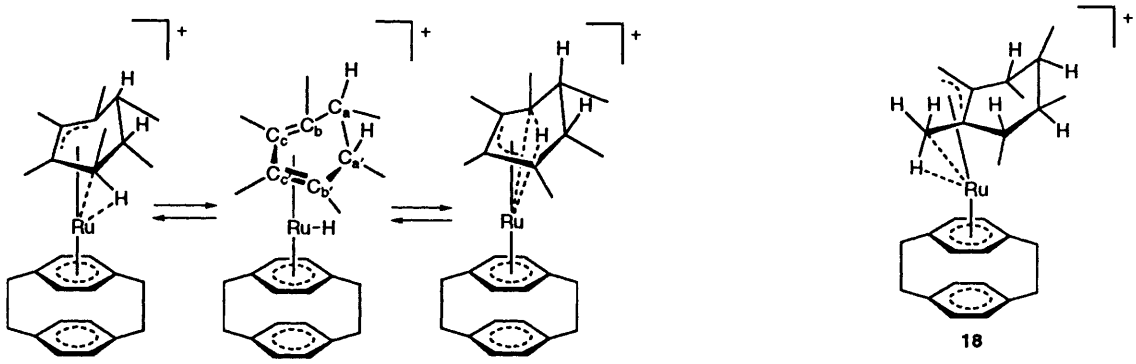


Fig. 5 Room temperature ^{1}H-coupled ^{13}C NMR spectrum of the fluxional agostic complex $[Ru(\eta^6\text{-}C_{16}H_{16})(\eta^3\text{-}C_6Me_6H_3)][BF_4]$ **16**



Scheme 3 Fluxionality in the agostic complex $[Ru(\eta^6\text{-}C_{16}H_{16})(\eta^3\text{-}C_6Me_6H_3)][BF_4]$ **16**

ordinated [2.2]paracyclophane deck was also barely visible as a broad peak in the baseline. Lowering the temperature even further resulted in the growth of a new set of signals strongly indicative of the loss of the dynamic plane of symmetry in the $C_6Me_6H_3$ ligand. At −135 °C four distinct resonances could be distinguished due to the methyl substituents on $C_{c'}$, C_c, $C_{b'}$ and C_b (δ 2.01, 1.62, 1.49 and 1.06 respectively). The latter peak exhibited traces of doublet coupling as expected in the static structure although the spectrum was rather broad as a consequence of precipitation and increasing solvent viscosity. Two signals were also observed for the two protons H_{exo} (δ 1.39 and 0.95) whilst the methyl substituents on C_a and $C_{a'}$ both occur at the same chemical shift (δ 0.61) near their averaged, room-temperature position.

The origins of the *exo* and agostic protons in **16** were confirmed by a series of deuteriation experiments. Reaction of the *exo*-dideuterio complex **4'** with HBF_4 led to the formation of the *exo*-dideuteriated agostic compound $[Ru(\eta^6\text{-}C_{16}H_{16})(\eta^3\text{-}C_6Me_6HD_2)][BF_4]$ **16'**. The *exo* nature of the deuterons was established by the observation of ν(CD) in the infrared spectrum at 2113 cm^{-1} and more importantly by the absence of the resonance due to H_{exo} in the ^{1}H NMR spectrum of the material (δ 1.22). Reaction of **4** with DBF_4 [synthesised by stirring HBF_4 (40% aq.) in D_2O] resulted in the *endo*-deuterio complex $[Ru(\eta^6\text{-}C_{16}H_{16})(\eta^3\text{-}C_6Me_6H_2D)][BF_4]$ **16"** which did not exhibit an obvious ν(CD) band in its infrared spectrum. The ^{1}H NMR spectrum of **16"** displayed a quartet resonance at δ 1.22 whilst the hydridic signal was *ca.* 40% of its intensity in the undeuteriated analogue **16**, as a result of protonation by residual HBF_4. Protonation of **4** was also carried out with CF_3CO_2D to give $[Ru(\eta^6\text{-}C_{16}H_{16})(\eta^3\text{-}C_6Me_6H_2D)][H(CF_3CO_2)_2]$ **17** which exhibited *ca.* 75% deuterium incorporation into the agostic site. The presence of the $[H(CF_3CO_2)_2]^-$ anion was confirmed by the observation of a resonance due to the acidic proton (resulting from H/D exchange during work up) in the ^{1}H NMR spectrum, δ 8.80, and signals for the trifluoroacetate carbon atoms in the ^{13}C NMR spectrum (Table 2).

Protonation of the 1,4-diene complex **2** with HBF_4 results in the formation of the agostic compound $[Ru(\eta^6\text{-}C_{16}H_{16})\{\eta^3\text{-}(HCH_2)(CH_2)C_6Me_4H_4\}][BF_4]$ **18** which is an isomer of **16** (FAB mass spectrum *m/z* 475, very little fragmentation). Complex **18** may be left in chloroform solution in air for several hours without appreciable decomposition and may be stored in air in the solid state for extended periods. Like **16**, the ^{1}H NMR spectrum of **18** is deceptively simple at room temperature. Two methyl resonances are observed, coupled to two 2 H multiplets assigned to H_d and H_e (for numbering scheme see Scheme 4) by selective homonuclear decoupling experiments [δ 0.95 (d, 6 H, ^3J = 6.6) and 0.82 (d, 6 H, ^3J = 6.8), CH_3; 2.08 (d of q, 2 H, ^3J = 4.9, 6.8, H_d) and 1.43 (d of q, 2 H, ^3J = 4.9, 6.6 Hz, H_e)]. A broad 5 H singlet was also observed at δ −1.52 which produces no change in the remaining resonances on selective irradiation. The singlet due to the co-ordinated cyclophane deck implies the existence of a dynamic plane of symmetry in the molecule.

Raising the temperature of the NMR probe to 50 °C results in a sharpening of the resonance at δ −1.52 confirming that the compound is in a fast-exchange regime. Low-temperature experiments down to −135 °C suggest that the complex is undergoing two dynamic processes (Scheme 4): (*a*) agostic CH exchange between the terminal sites $C_a/C_{a'}$ (analogous to the dynamic process described for **16**) resulting in the molecule exhibiting a dynamic plane of symmetry at higher temperatures and (*b*) agostic methyl group rotation resulting in the averaging of the signals for H_a, H_b and H_c.

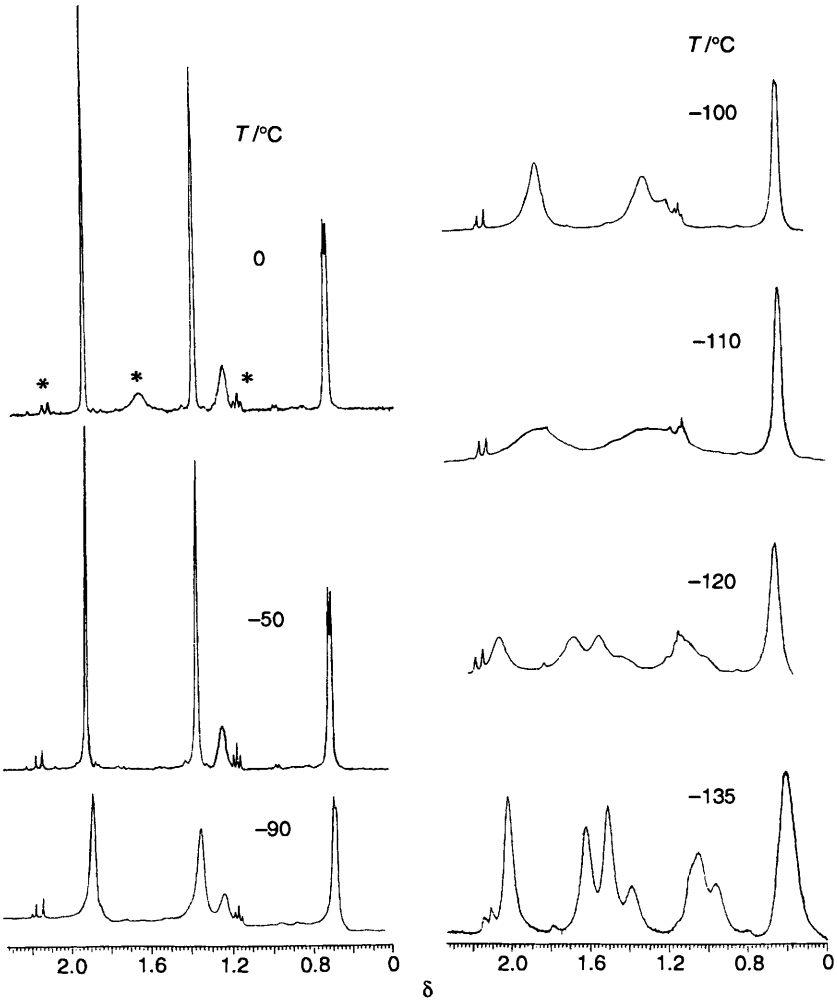
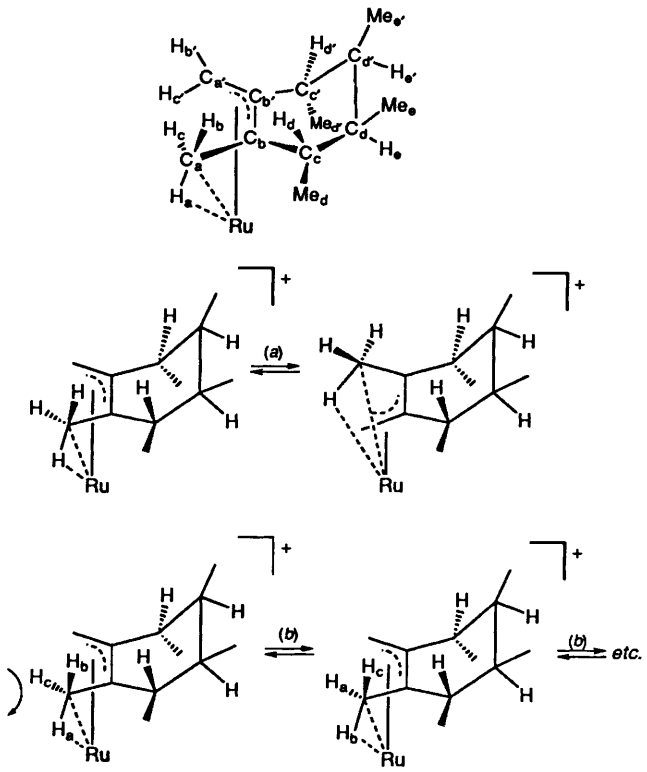


Fig. 6 Partial variable-temperature ^{1}H NMR spectra of [Ru(η^6-$C_{16}H_{16}$)(η^3-$C_6Me_6H_3$)][BF_4] **16**. Peaks marked (*) are due to impurities

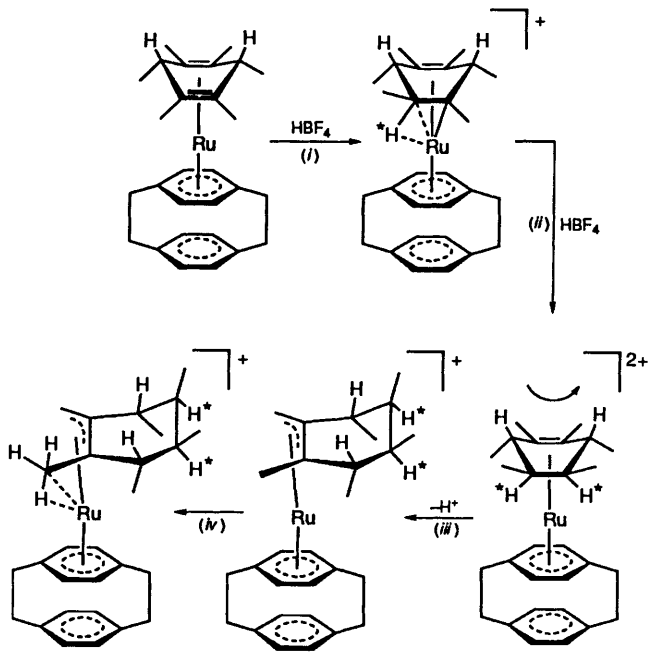
The slower of these dynamic exchanges is process (*b*), agostic methyl rotation. At −50 °C the 5 H resonance at δ −1.52 was replaced by two broad signals at δ −0.90 (2 H) and −9.92 (1 H). A further 2 H resonance would be expected in the region of δ *ca.* 2.5 but was apparently too broad to be observable at this temperature. The resonance at δ −9.92 occurs at a very similar chemical shift to the agostic signal for C_b–H in **16** and by analogy is assigned to the agostic proton H_a whilst the resonance at δ −0.90 probably corresponds to the *syn* protons H_c and $H_{c'}$. At this temperature the resonance due to the protons of the co-ordinated deck of the cyclophane ligand remained a sharp singlet implying that the molecule retains a dynamic plane of symmetry. Lowering the temperature to −80 °C results in the sharpening of the 'hydridic' resonance due to H_a and its splitting into a quintet consistent with coupling to all four protons H_b, $H_{b'}$, H_c and $H_{c'}$ confirming the freezing out of process (*b*) although not process (*a*). In addition, between −50 and −80 °C the resonance at δ −0.90 disappears once more to be replaced by two broad 1 H signals at δ 0.10 and −1.85 whilst the resonances due to Me_d/$Me_{d'}$ and the *endo* protons H_e/$H_{e'}$ as well as the signal for the co-ordinated cyclophane deck broaden significantly. At −100 °C, process (*a*) is also slow on the NMR timescale and the loss of the dynamic plane of symmetry is reflected by the splitting of the resonances due to the co-ordinated deck of the cyclophane ligand into two broad signals (δ 5.10 and 4.65). The hydridic resonance at δ −9.92 now occurs as a triplet due to coupling to H_b and H_c (δ 0.10 and −1.85 respectively) with a $^2J_{HH}$ = *ca.* 14 Hz, consistent with geminal coupling (unlike $^1J_{CH}$, no reduction is expected in $^2J_{HH}$ in agostic systems[37]). The *exo* protons H_d and $H_{d'}$ occurred at δ 2.18 and 2.09 whilst the difference in chemical shift of the *endo* protons H_e and $H_{e'}$ was somewhat larger (δ 1.59 and 1.26). The *anti* olefinic proton $H_{b'}$ was masked by the signals for the cyclophane ethylenic bridges, whilst $H_{c'}$ was observed at δ 0.67. All four methyl groups were also unique (δ 0.99, 0.96, 0.89 and 0.52).

These results contrast sharply with the fluxional processes observed by Bennett *et al.*[29] in the closely related agostic diphosphine compound [Ru{η^3-$(HCH_2)(CH_2)C_6Me_4$}{(*Z*)-$Ph_2PCH{=}CHPPh_2$}(PMe_2Ph)][PF_6] and related examples. In these complexes agostic methyl rotation [analogous to process (*b*) in **18**] is extremely rapid and could not be frozen out at temperatures down to −90 °C, the protons analogous to $H_{a,b,c}$ occurring as a 3 H multiplet at δ −2.20. In contrast, the process of type (*a*) (metal–hydride mediated exchange of H_a between the two terminal olefinic sites C_a and $C_{a'}$) was *slow* on the NMR time-scale at temperatures below +60 °C. These large differences in exchange rates may be rationalised by arguing that the agostic interaction in **18** is much stronger than in the *o*-xylylene–phosphine analogues,[29] where long-range interactions between the unco-ordinated, endocyclic olefinic functionalities may serve to provide additional stabilisation to the metal centre. A stronger agostic interaction would inhibit methyl group rotation [process (*b*)] because M–H bond breaking is involved, whilst process (*a*) would be facilitated as a consequence of the more hydridic nature of the M–H bond and corresponding weakening of the C–H_a interaction.

Further evidence for the agostic nature of **18** comes from its room-temperature ^{1}H-coupled ^{13}C NMR spectrum (Table 2). Consistent with the proposed formulation, the unsaturated ring carbon atoms C_b/$C_{b'}$ exhibit a singlet resonance at δ 100.62



Scheme 4 Fluxionality in the agostic complex $[Ru(\eta^6\text{-}C_{16}H_{16})\{\eta^3\text{-}(HCH_2)(CH_2)C_6Me_4H_4\}][BF_4]$ **18**; (*a*) terminal agostic exchange and (*b*) methyl rotation

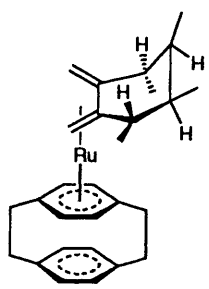


Scheme 5 Proposed mechanism for the formation of the agostic complex $[Ru(\eta^6\text{-}C_{16}H_{16})\{\eta^3\text{-}(HCH_2)(CH_2)C_6Me_4H_4\}][BF_4]$ **18** (starred atoms originate from $H[BF_4]$)

whereas the sp^3 carbons C_c, $C_{c'}$, C_d and $C_{d'}$ display two doublet signals at typically aliphatic chemical shifts with one bond coupling constants consistent with non-agostic binding of the ring hydrogen atoms (δ 36.62 and 36.06, $^1J_{CH}$ = *ca.* 127 Hz). Similarly, two quartet resonances exhibiting typically aliphatic couplings are observed for Me_c and Me_d. A further broad quartet (δ 17.45, $^1J_{obs}$ = 77.5 Hz), is also observed with a significantly reduced observed coupling constant which again represents an average value over the dynamic processses described above. This resonance is assigned to the agostic methyl carbon atoms C_a and $C_{a'}$.

The structure of **18** is a surprising one and we propose the mechanism of its formation from **2** to be of the type shown in Scheme 5. Steps (*i*)–(*iv*) are shown as sequential but since this would involve a 14-electron intermediate the mechanism is probably concerted and involves further agostic stabilisation. Step (*i*) consists of protonation and oxidation of the metal centre followed by partial hydride transfer to the organic ligand to give an unstable ene-yl intermediate analogous to **16**. Unlike **16** however, the complex undergoes a second protonation (*cf.* the facile double reprotonation of **13** to regenerate **1e**) to relieve the strain inherent in the intermediate ene-yl structure [step (*ii*)] resulting in a formally 14-electron dicationic complex. This second protonation could occur in either an *exo* or *endo* fashion but is apparently *endo* since an *exo* protonation would result in H_e and $H_{e'}$ being inequivalent even in a fast-exchange regime. In step (*iii*) the dicationic intermediate rapidly deprotonates at one of the methyl groups on the opposite side of the molecule to give a more stable 16-electron allyl complex and finally [step (*iv*)] the metal attains an 18-electron configuration by a new agostic interaction with the methyl group adjacent to the newly formed exocyclic allylic functionality.

In an attempt to establish the validity of this mechanism we attempted the preparation of the dideuterio analogue of **2**, $[Ru(\eta^6\text{-}C_{16}H_{16})(\eta^4\text{-}3,6\text{-}C_6Me_6D_2)]$ **2'** from the reaction of **1e** with $Na[BD_4]$. In favourable cases, in the absence of aqueous



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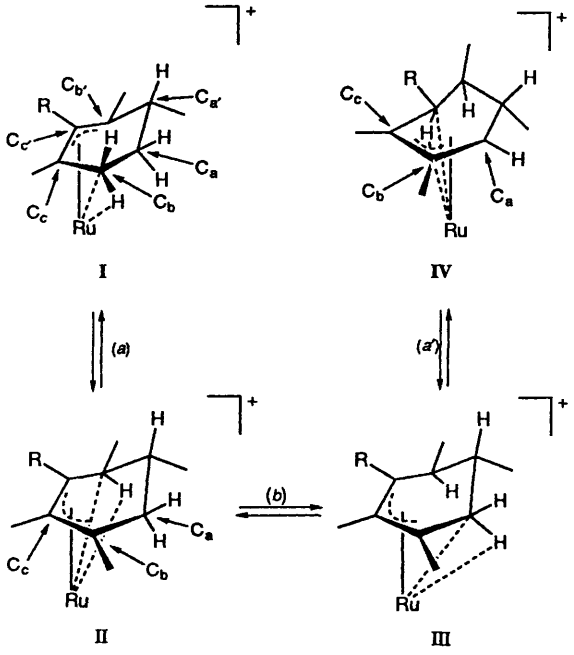
quenching, *ca.* 2:1 mixtures of **4'** and **2'** could be generated. Due to the air sensitivity of the (diene)ruthenium(0) complexes these mixtures were not separated but were protonated with HBF_4 to give approximately 5:1 mixtures of **16'** and the *exo* dideuterio analogue of **18**, $[Ru(\eta^6\text{-}C_{16}H_{16})\{\eta^3\text{-}(HCH_2)(CH_2)C_6Me_4H_2\text{-}D_2\}][BF_4]$ **18'**. In spite of the low relative concentration of **18'**, the ^1H NMR spectrum of the mixture clearly demonstrated the inclusion of deuterons exclusively at H_d and $H_{d'}$ consistent with the suggestion that H_e and $H_{e'}$ both come from the HBF_4.

Deprotonation of **18** with $LiBu^n$ results in the rapid formation of a further isomer of **2** and **4**, namely $[Ru(\eta^6\text{-}C_{16}H_{16})\text{-}\{\eta^4\text{-}(CH_2)_2C_6Me_4H_4\}]$ **19**, in 89% yield. Firm evidence for the binding of the metal centre to exocyclic olefinic functionalities comes from the relatively high field chemical shifts of the *anti* and *syn* $=CH_2$ protons which resonate at δ 1.45 and −0.71 respectively [*cf.* the unbound exocyclic olefinic functionalities in **13** (δ 4.64 and 4.20)]. The remainder of the ^1H NMR spectrum of **19** strongly resembles the room-temperature spectrum of **18** and provides good evidence for the proposed formulation.

Reaction of the pentamethyl and tetramethyl complexes **6** and **7** with HBF_4 also results in the formation of agostic protonolysis products $[Ru(\eta^6\text{-}C_{16}H_{16})(\eta^3\text{-}C_6Me_{5-n}H_{4+n})]\text{-}[BF_4]$ (n = 0, **20**; 1, **21**). Consistent with the proposed 1,3-diene structures of **6** and **7**, the metal atoms in **20** and **21** are co-ordinated *via* endocyclic allylic functionalities. All the methyl groups in both compounds are magnetically unique in their ^1H NMR spectra with only one in each case exhibiting low averaged $^3J_{HH}$ [δ 1.05 ($^3J_{obs}$ = 4.8), **20**; 0.91 ($^3J_{obs}$ = 5.8), **21**;



Scheme 6 Fluxionality in the agostic complexes $[Ru(\eta^6\text{-}C_{16}H_{16})(\eta^3\text{-}C_6Me_{5-n}H_{4+n})][BF_4]$ (n = 0, **20**; 1, **21**): (*a*), (*a'*) exchange of agostic proton and (*b*) transfer of agostic interaction

cf. 6.7 and 6.4 Hz for the methyl groups coupled to H_{exo} in the same compounds]. The co-ordinated deck of the paracyclophane ligands occur as AA'BB' quartets consistent with the asymmetric structures of the complexes. More importantly, both complexes exhibit two broad high field resonances in their room-temperature ^1H NMR spectra indicating that both *endo* protons are involved in agostic interactions. In the case of **20** these protons occur at similar chemical shifts (δ −4.56 and −5.25) and it would seem likely that each spends an approximately equal proportion of their time in agostic co-ordination to the metal centre. In contrast, one resonance in compound **21** occurs at much higher field than the other (δ −7.68 *cf.* −1.88) indicating a strong thermodynamic preference for agostic binding on one side of the asymmetric organic ligand. Moreover, the remainder of the ^1H NMR spectrum of **21**, in conjunction with homonuclear decoupling experiments, indicates that the highest field resonance is assignable to the *endo* proton of the CH_2 (as opposed to CHMe) group and does not correspond to the proton ostensibly from the HBF_4 (although the actual origins of each of the *endo*-hydrogen atoms is likely to be unknowable as a result of rapid scrambling). These results are summarised in Scheme 6 which presents the two fluxional processes [processes (*a*) and (*b*)] responsible for the observed exchange in **20** and **21**. Protonation of **6** and **7** doubtless proceeds initially in a manner analogous to that observed for **4** to give a complex of type **I** or type **II** analogous to **16**, which equilibrate *via* H-atom exchange between the terminal olefinic sites. Because of the availability of a second *endo*-hydrogen atom however, complexes of type **II** may access another, non-degenerate structure [type **III**, process (*b*)] involving interaction of the metal centre with a different C–H bond. Like those of type **II**, molecules of type **III** may also undergo exchange of the agostic proton between terminal olefinic sites [process (a')] to give complexes of type **IV**. In the case of **20** the *exo*-methyl substituent on one side of the molecule makes only a slight difference to the donor abilities of one C–H bond over the other and so molecules of type **I**/**II** and type **III**/**IV** are present in roughly equimolar amounts. In contrast, equilibrium (*b*) in the case of **21** significantly favours molecules of type **III**/**IV** with the *endo* proton of the CH_2 group taking part in an agostic interaction with the metal centre. Such a preference may be rationalised in terms of the relative π-donor abilities of the allylic functionality in complexes of type **II** and **III**. In the case of **20** all three allylic carbon atoms (C_b, C_c and $C_{c'}$) are methylated and undoubtedly C_b and $C_{c'}$ have similar donor abilities. In **21** however, there is no methyl substituent on $C_{c'}$ and C_b is therefore likely to be the better donor of the two. Hence the relatively electron deficient metal centre is more stabilised in complexes of type **III**, in which it is situated on the more electron rich side of the organic ligand. The geometries of complexes **20** and **21** and the nature of the exchange processes involved have been confirmed by ^{13}C and variable-temperature ^1H NMR spectroscopy.

Raising the temperature of the NMR probe to +50 °C results only in a sharpening of the two high-field ^1H NMR resonances implying rapid dynamic exchange. Between 0 and −80 °C all the resonances except those due to the methyl groups bonded to C_c and $C_{a'}$ in both **20** and **21** broaden markedly. At −80 °C the resonances corresponding to the two agostic protons in **20** (δ −4.56 and −5.25) have been replaced by two new signals in a ratio of *ca.* 3:4 (δ −10.55 and −11.01) close to the chemical shifts observed for the agostic protons in **16** and **18**. At −100 °C these signals sharpen with one (δ −10.55) exhibiting a doublet structure $^2J_{HH}$ = *ca.* 9 Hz consistent with the *endo* proton of the C_aH_2 group. The resonance at δ −11.01 should be a quartet, corresponding to the *endo* proton of the $C_{b'}HMe$ section of the ring but the coupling is not resolved. Similarly the remainder of the spectrum of **20** is split into two sets of resonances with even two sets of AA'BB' type resonances being observed of the protons of the co-ordinated cyclophane deck and a total of ten signals (allowing for the accidental overlap of some resonances) for the methyl substituents of the agostic ligand. These observations suggest that at −100 °C both processes (*a*) and (*b*) are slow and two isomers of **20** have been resolved corresponding to the structures shown as types **II** and **III** in Scheme 6. Consistent with the room-temperature ^1H and ^{13}C NMR (see below) data the isomers are of similar energy and are present in approximately equimolar amounts at low temperature. Signals assignable to structures **I** and **IV** were not observed at low temperature indicating that these are less stable.

In contrast to **20**, the ^1H NMR spectrum of **21** at −80 °C indicates the presence of only a single isomer. The chemical shift and coupling constant of the agostic resonance is consistent with the type **III** structure.

The room-temperature ^1H-coupled ^{13}C spectra of **20** and **21** (Table 2) are also consistent with the proposed geometries. In the case of **20** the resonance due to $C_{a'}$ (δ 34.34) occurs as a doublet with a typical aliphatic coupling constant whilst the resonances due to $C_{b'}$ and C_a [δ 52.76 (d, J_{obs} = 87.0) and 41.94 (dd, J_{obs} = 95.5, 141.2 Hz) respectively] exhibit agostic couplings to the *endo* protons. The similarity in the magnitudes of these two couplings is consistent with there being little thermodynamic preference between species of type **II** and type **III** in **20**. The slightly lower value of $^1J_{obsC_{b'}\text{-}H}$ is consistent with the higher field chemical shift of this hydrogen atom in the ^1H spectrum and implies that agostic interaction at $C_{b'}$–H (type **I**/**II**) is a marginally more significant mode of co-ordination. In **21** the situation is reversed [$^1J_{obsC_{b'}H}$ = 101.6, $^1J_{obsC_aH}$ = 69.1 Hz], and the preference is for agostic interaction at C_a–H. As might be expected the ^{13}C NMR spectra of **20** and **21** are very similar to one another in most other respects with the only other striking dissimilarity being the chemical shifts of the resonances assigned due to $C_{c'}$ in the two complexes. In **20** $C_{c'}$ bears a methyl substituent and is observed at δ 73.83. In **21** the resonance occurs as a doublet (δ 64.30, ^1J = 161.0 Hz) consistent with the hydrogen atom substituent but, counterintuitively, at a relatively *upfield* chemical shift. Clearly the different shielding effects of R = H/Me is outweighed by the fact that in **21** there is a significant contribution to the average environment of this carbon atom by the type **IV** geometry in which it adopts an sp^3 hybridisation and consequently resonates at a significantly more aliphatic chemical shift. Further evidence for the complexes spending part of their time as structure **IV** comes

Table 2 Proton coupled ^{13}C NMR data for agostic compounds[a]

	Compound	δ			
		Ring	Bridgehead	Bridge	Ligand
16	$[Ru(\eta^6\text{-}C_{16}H_{16})(\eta^3\text{-}C_6Me_6H_3)][BF_4]$	133.43 (d, J = 160.8), 82.18 (d, J = 174.6)	139.08 (s) 125.07 (s)	34.22 (t, J = 131.2), 31.35 (t, J = 129.9)	91.51 (s, C_c, $C_{c'}$), 59.25 (d, J = 36.0 av., C_b, $C_{b'}$), 38.45 (d, J = 129.8 av., C_a, $C_{a'}$), 20.43 (q, J = 127.6, CH_3), 15.47 (q, J = 128.0, CH_3), 13.20 (q, J = 126.8, CH_3)
16′	$[Ru(\eta^6\text{-}C_{16}H_{16})(\eta^3\text{-}C_6Me_6HD_2)][BF_4]$	133.40 (d, J = 158.1), 82.12 (d, J = 176.1)	139.06 (s) 124.96 (s)	34.12 (t, J = 131.1), 31.24 (t, J = 132.5)	91.41 (s, C_c, $C_{c'}$), 59.03 (d, J = 37.5 av., C_b, $C_{b'}$), 37.79 (s,[b] C_a, $C_{a'}$), 20.32 (q, J = 128.6, CH_3), 15.38 (q, J = 128.2, CH_3), 13.20 (q, J = 126.4, CH_3)
16″	$[Ru(\eta^6\text{-}C_{16}H_{16})(\eta^3\text{-}C_6Me_6H_2D)][BF_4]$	133.45 (d, J = 158.3), 82.08 (d, J = 178.4)	139.06 (s) 124.99 (s)	34.15 (t, J = 130.4), 31.27 (t, J = 131.2)	91.50 (s, C_c, $C_{c'}$), 59.28 (s,[b] C_b, $C_{b'}$), 38.36 (d, J = 130.3 av., C_a, $C_{a'}$), 20.32 (q, J = 128.6, CH_3), 15.43 (q, J = 128.2, CH_3), 13.18 (q, J = 126.7, CH_3)
17	$[Ru(\eta^6\text{-}C_{16}H_{16})(\eta^3\text{-}C_6Me_6H_2D)][H(CF_3CO_2)_2]$	133.32 (d, J = 158.3), 82.00 (d, J = 174.8)	159.82 (s) 125.16 (s)	34.16 (t, J = 131.6), 31.28 (t, J = 132.8)	160.37 [q, $^2J_{CF}$ = 36.8, $H(CF_3CO_2)_2$], 116.20 [q, $^1J_{CF}$ = 289.7, $H(CF_3CO_2)_2$], 91.54 (s, C_c, $C_{c'}$), 58.90 (s,[b] C_b, $C_{b'}$), 38.32 (d, J = 130 av., C_a, $C_{a'}$), 20.35 (q, J = 127.4, CH_3), 15.38 (q, J = 128.2, CH_3), 13.13 (q, J = 126.4, CH_3)
18	$[Ru(\eta^6\text{-}C_{16}H_{16})\{\eta^3\text{-}(HCH_2)(CH_2)C_6Me_4H_4\}][BF_4]$	133.35 (d, J = 158.2), 80.66 (d, J = 176.4)	139.01 (s) 125.53 (s)	34.52 (t, J = 132.9), 33.20 (t, J = 137.5)	100.62 (s, C_b, $C_{b'}$), 36.62 (d, J = 128.7, C_c, $C_{c'}$), 36.06 (d, J = 127.0, C_d, $C_{d'}$), 20.77 (q, J = 127.3, Me_c, $Me_{c'}$), 17.45 (q, br, J = 77.5 av., C_a, $C_{a'}$), 15.94 (dq, J = 125.2, 3.6, Me_d, $Me_{d'}$)
20	$[Ru(\eta^6\text{-}C_{16}H_{16})(\eta^3\text{-}C_6Me_5H_4)][BF_4]$	133.43 (d, J = 157.6), 82.85 (d, J = 175.4), 82.43 (d, J = 175.5)	139.07 (s) 125.30 (s)	34.20 (t, J = 132.0), 31.40 (t, J = 132.0)	91.19 (s, C_c, 80.67 (s, C_b), 73.83 (s, $C_{c'}$), 52.76 (d, J = 87.0 av., $C_{b'}$), 41.94 (dd, J = 95.5, 141.2 av., C_a), 34.34 (d, J = 128.8, $C_{a'}$), 21.62 (q, J = 128.2, CH_3), 19.27 (q, J = 126.5, CH_3), 19.10 (q, J = 125.8, CH_3), 18.55 (q, J = 128.2, CH_3), 14.91 (q, J = 128.2, CH_3)
21	$[Ru(\eta^6\text{-}C_{16}H_{16})(\eta^3\text{-}C_6Me_4H_5)][BF_4]$	133.45 (dd, J = 158.6, 5.0), 82.21 (dd, J = 176.3, 6.2), 81.36 (dd, J = 175.2, 6.1)	139.08 (s) 126.05 (s)	34.41 (t, J = 128.8), 31.79 (t, J = 131.4)	90.20 (s, C_c), 80.67 (s, C_b), 64.30 (d, J = 161.0, $C_{c'}$), 48.24 (d, J = 101.6, $C_{b'}$), 42.88 (dd, J = 143.6, 69.1, C_a), 34.25 (d, J = 128.2, $C_{a'}$), 21.36 (q, J = 128.5, CH_3), 19.77 (q, J = 127.4, CH_3), 19.56 (q, J = 128.3, CH_3), 18.59 (q, J = 128.2, CH_3)

[a] Solvent $CDCl_3$ unless otherwise stated, 100.6 MHz, 298 K, J_{CH} in Hz, δ in ppm, s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, dq = doublet of quartets, br = broad; [b] $^1J_{CD}$ unresolved.

from the signals due to the aliphatic carbon atoms C_a in **20** and **21** which exhibit an unexpectedly high coupling to one of the *exo* protons [141.2 (**20**) and 143.6 (**21**) Hz], possibly indicative of a partial olefinic character. The suggestion is supported by the relatively high chemical shifts of these resonances (δ 41.94 and 42.88 respectively), suggesting that the carbon atoms spend some time in an sp^2 state of hybridisation, as expected from the occurrence of process (a') and the accessing of structure **IV** [*cf.* $C_{a'}$ δ 34.34 (J_{obs} = 128.8), **20** and 34.25 (J_{obs} = 128.2), **21**].

Conclusion

Incorporation of [2.2]paracyclophane in complexes of the form $[Ru(arene)(arene')]^{2+}$ as a non-innocent spectator ligand results in the observation of reactions in which the selective double nucleophilic addition of hydride to the non-cyclophane ring can occur with a high degree of regioselectivity, which may be tuned by judicious choice of reaction conditions. The resulting (diene)ruthenium(0) complexes react with sources of H^+ to give a range of interesting agostic species which might be oxidatively cleaved to give unusual organic cyclohexenes. Attempts to extend the synthetic approach to generate functionalised diene species from attack by nucleophiles other than hydride are complicated by the formation of complex mixtures of products and the relatively poor electrophilicity of the more highly alkylated arenes.

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References

1 D. Astruc, *New J. Chem.*, 1992, **17**, 305.
2 D. Astruc, *Top. Curr. Chem.*, 1991, **160**, 47.
3 M. Uemura, T. Minami, Y. Shinoda, H. Nishimura, M. Shiro and Y. Hayashi, *J. Organomet. Chem.*, 1991, **406**, 371.
4 M. Uemura, H. Nishimura, T. Minami and Y. Hayashi, *J. Am. Chem. Soc.*, 1991, **113**, 5402.
5 C. C. Neto and D. A. Sweigart, *J. Chem. Soc., Chem. Commun.*, 1990, 1703.
6 Y.-K. Chung, E. D. Honig and D. A. Sweigart, *J. Organomet. Chem.*, 1983, **256**, 277.
7 M. A. Bennett and T. W. Matheson, *J. Organomet. Chem.*, 1979, **175**, 87.
8 M. I. Rybinskaya, A. R. Kudinov and V. S. Kaganovich, *J. Organomet. Chem.*, 1983, **246**, 279.
9 S. G. Davies, M. L. H. Green and D. M. P. Mingos, *Tetrahedron*, 1978, **34**, 3047.
10 T. S. Cameron, M. D. Clerk, A. Linden, K. C. Sturge and M. J. Zaworotko, *Organometallics*, 1988, **7**, 2571.
11 J. F. Helling and G. G. Cash, *J. Organomet. Chem.*, 1974, **73**, C10.
12 D. R. Robertson, I. W. Robertson and T. A. Stephenson, *J. Organomet. Chem.*, 1980, **202**, 309.
13 D. N. Cox and R. Roulet, *Organometallics*, 1986, **5**, 1886.
14 J. Müller and S. Schmitt, *J. Organomet. Chem.*, 1975, **97**, 275.
15 V. S. Kaganovich, A. R. Kudinov and M. I. Rybinskaya, *J. Organomet. Chem.*, 1987, **323**, 111.
16 H. LeBozec, D. Touchard and P. H. Dixneuf, *Adv. Organomet. Chem.*, 1989, **29**, 163.
17 J. W. Steed and D. A. Tocher, *J. Organomet. Chem.*, 1991, **412**, C37.
18 M. R. J. Elsegood, J. W. Steed and D. A. Tocher, *J. Chem. Soc., Dalton Trans.*, 1992, 1797.
19 R. T. Swann, A. W. Hanson and V. Boekelheide, *J. Am. Chem. Soc.*, 1986, **108**, 3324.
20 J. W. Steed and D. A. Tocher, *J. Organomet. Chem.*, 1993, **444**, C47.
21 M. A. Bennett and A. K. Smith, *J. Chem. Soc., Dalton Trans.*, 1974, 233.
22 P. Michaud, A. Madonik, J.-Y. Saillard and R. Hoffman, *Nouv. J. Chim.*, 1985, **9**, 41.
23 A. L. Burrows, B. F. G. Johnson, J. Lewis and D. G. Parker, *J. Organomet. Chem.*, 1980, **194**, C11.
24 R. D. Pike, W. J. Ryan, N. S. Lennhoff, J. Van Epp and D. A. Sweigart, *J. Am. Chem. Soc.*, 1990, **112**, 4798.
25 M. R. J. Elsegood, Ph.D. Thesis, University College London, 1991.
26 J. W. Hull, C. Mann and W. L. Gladfelter, *Organometallics*, 1992, **11**, 3117.
27 J. W. Hull and W. J. Gladfelter, *Organometallics*, 1982, **1**, 1716.
28 J. W. Hull, K. J. Roesselet and W. L. Gladfelter, *Organometallics*, 1992, **11**, 3630.
29 M. A. Bennett, L. Y. Goh, I. J. McMahon, T. R. B. Mitchell, G. B. Robertson, T. W. Turney and W. A. Wickramasinghe, *Organometallics*, 1992, **11**, 3069.
30 H. Werner and R. Werner, *J. Organomet. Chem.*, 1979, **174**, C67.
31 H. Werner and R. Werner, *Angew. Chem.*, 1978, **90**, 721.
32 H. Werner and R. Werner, *Chem. Ber.*, 1982, **115**, 3781.
33 M. Brookhart, M. L. H. Green and L.-L. Wong, *Prog. Inorg. Chem.*, 1988, **36**, 1.
34 W. W. Paudler, *Nuclear Magnetic Resonance*, Wiley, New York, 1987, p. 147.
35 M. Brookhart, W. Lamanna and M. B. Humphrey, *J. Am. Chem. Soc.*, 1982, **104**, 2117.
36 M. A. Bennett and T. W. Matheson, *J. Organomet. Chem.*, 1978, **153**, C25.
37 M. L. H. Green, A. K. Hughes, N. A. Popham, A. H. H. Stephens and L.-L. Wong, *J. Chem. Soc., Dalton Trans.*, 1992, 3077.

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