Synthesis of ruthenium(0) dienes from \([2\text{-}2]\)paracyclophane)(arene) ruthenium(II) complexes and their subsequent reactions to form highly fluxional agostics

J W STEED and D A TOCHER*

Department of Chemistry, University College London, 20 Gordon Street, London WC1H 0AJ, UK

Abstract. Action of Na\([\text{BH}_4]\) on the \((2\text{-}2)\)Paracyclophane)(arene)ruthenium(II) complexes \([\text{Ru}(\sigma^6\text{-C}_{16}\text{H}_{16})(\eta^6\text{-arene})][\text{BF}_4]\) \(, \text{arene}=p\) -cymene 1a, durene 1b, pentamethylbenzene 1c, and hexamethylbenzene 1d) results exclusively in reduction of the metal centre and addition of two hydrides to the non-cyclophane ring, giving the neutral 1,3-diene compounds \([\text{Ru}(0)(\sigma^6\text{-C}_{16}\text{H}_{16})(\eta^4\text{-diene})][\text{BF}_4]\) \(, \text{diene}=\text{MeC}_6\text{H}_4\text{CHMe}_2 \ 2a, \ C_6\text{Me}_4\text{H}_4 \ 2b, \ C_6\text{Me}_5\text{H}_3 \ 2c, \ C_6\text{Me}_6\text{H}_2 \ 2d). These results contrast with several previous studies on Ru(II) bis(arene) cations in which reaction to form bis(cyclohexadienyls) is often observed. Compounds 2b, 2c, and 2d react with H\([\text{BF}_4]\) to generate a series of fluxional agostic ruthenium(II) cyclohexenyl compounds \([\text{Ru}(\sigma^6\text{-C}_{16}\text{H}_{16})(\eta^3\text{-C}_6\text{Me}_n\text{H}_{9-n})][\text{BF}_4]\) \(, \text{n}=4, \ 3b; \ 5, \ 3c; \ 6, \ 3d). In each of these complexes the agostic cyclohexenyl ligand is bound via an endocyclic allylic functionality. However, an isomer of 3d, \([\text{Ru}(\sigma^6\text{-C}_{16}\text{H}_{16})(\eta^3\text{-}(\text{HCH}_2)(\text{CH}_2)\text{C}_6\text{Me}_n\text{H}_{11})][\text{BF}_4]\), in which the metal is bound externally to the ring is formed in the reaction of the 1,4-diene compound \([\text{Ru}(\sigma^6\text{-C}_{16}\text{H}_{16})(\eta^4\text{-3,6-C}_6\text{Me}_6\text{H}_2})\] with H\([\text{BF}_4]\). The mechanisms of formation of these compounds have been probed by deuteration studies and their extensive dynamic behaviour investigated by variable temperature \(^1\text{H}\) NMR spectroscopy.

Keywords. Ruthenium(0); regioselectivities; endo hydrogen atom; agostic interaction.

1. Introduction

Nucleophilic addition reactions to coordinated arene rings are of significant interest and practical viability in arene and diene functionalisation (Neto and Sweigart 1990; Astruc 1991, 1992; Uemura et al 1991). Bis(arene) complexes of ruthenium(II) are of special relevance in this context because of their high stability and lack of air and moisture sensitivity. Although somewhat less electrophilic than their iron analogues (Chung et al 1983), 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 (Neto and Sweigart 1990; Uemura et al 1991). Moreover, a wide range of unsymmetrical bis(arene)ruthenium complexes are available via the routes of Bennett (Bennett and Matheson 1979) and Rybinskaya (Rybinskaya et al 1983), unlike the iron analogues.

Single nucleophilic addition reactions give rise to functionalised cyclohexadienyl complexes (Helling and Cash 1974; Davies et al 1978; Robertson et al 1980; Cameron

*For correspondence
et al 1988) from which functionalised arenes may be generated by hydride abstraction (Müller and Schmitt 1975; Cox and Roulet 1986). Double nucleophilic additions to [Ru(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 (Kaganovich et al 1987; LeBozec et al 1989), give rise to bis(cyclohexadienyl) complexes even when one of the arenes is the sterically congested 1,3,5-triisopropylbenzene ligand (Neto and Sweigart 1990).

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 coordinated to the same metal centre, even in the case of poorly electrophilic arenes such as hexamethylbenzene (Steed and Tother 1991; Elsegood et al 1992). It is also noteworthy that Boekelheide (Swann et al 1986) has demonstrated that the action of the hydride source red-Al upon [Ru(η⁶-[2·2]paracyclophane)(η⁶-arene)][BF₄]₂ (arene = C₆H₆ and C₆Me₆) gives solely diene products.

We now report the synthesis of a range of (diene)ruthenium(0) complexes by the double nucleophilic addition of (arene)ruthenium(II) complexes containing [2·2] paracyclophane as a spectator ligand and discuss the reactivity of these complexes towards H[BF₄] (Steed and Tocher 1993).

2. Results and discussion

2.1 Diene ruthenium(0) complexes

Work by Boekelheide (Swann et al 1986) has shown that the reduction of the hexamethylbenzene complex [Ru(η⁶-C₁₆H₁₆)(η⁶-C₆Me₆)][BF₄]₂, 1d, with red-Al [sodium bis(methoxyethoxy) aluminium hydride] gives the cyclohexa-1,4-diene ruthenium(0) compound [Ru(η⁶-C₁₆H₁₆)(η⁴-exo, exo-3,6-C₆Me₆H₂)]. Conversely,
the analogous reduction of the benzene complex results in the formation of a cyclohexa-1,3-diene complex $[\text{Ru}(\eta^5-C_{16}H_{16})(\eta^4-5,6-C_6H_8)]_3$. 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 1a (Swann et al. 1986). 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 are frontier molecular orbitally controlled, and result from 1,2-double addition (Astruc 1985, 1991, 1992).

Surprisingly, on carrying out the sodium borohydride reduction of 1d we find that the 1,3-diene 2d is formed as the sole product. This complex is readily identified by its $^1$H NMR spectrum which exhibits a singlet resonance for the coordinated deck of the paracyclophane ligand at $\delta$ 4.09, a chemical shift characteristic of a neutral ruthenium(0) species (cf. complex 2: $\delta$ 3.95). Three methyl resonances are observed, and a quartet for the exo hydrogen atoms [$\delta$ 1.74, 1.10 and 0.56 ($d$, $^3J = 6.8$), CH$_3$;
1.18 (q, $^3J = 6.8$ ppm, exo-H]. The infrared spectrum of 2d exhibits a strong band due to $\nu$(CH$_{\text{exo}}$) at 2808 cm$^{-1}$, shifting to 2083 cm$^{-1}$ in the deuterium complex $[\text{Ru}(\eta^6-C_{16}H_{16})(\eta^5-\text{exo, exo-}5,6-C_6\text{Me}_6D_2)]$ confirming exo addition.

Complex 2d is structurally similar to a wide range of (1,3-diene)iron(0) species formed by direct 1,2-double addition under conditions of frontier orbital control (Astruc 1985, 1991, 1992). The question as to whether 2d is formed as a consequence of direct 1,2-double addition (scheme 1b) or results from the rearrangement of a 1,4-diene, formed initially, followed by a intramolecular [1,3]- or series of [1,2]-sigmatropic shifts (scheme 1c) has important consequences for the validity of the charge-controlled model for nucleophilic additions to ruthenium.

It should also be mentioned that the formation and isolation of 2d is sensitive to aqueous quenching. If water is not added to destroy Na[BH$_4$] during work-up then approximately 20–30% of the isolated product takes the form of the 1,4-diene. It is notable that aqueous quenching was a necessary feature of Boekelheide's procedure for the formation of the 1,4-diene using the reducing agent red-Al.

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 $[\text{Ru}(\eta^6-C_{16}H_{16})(\eta^6-\text{arene})][\text{BF}_4]_2$ compounds (arene = p-cymene 1a, durene 1b and pentamethylbenzene 1c). In the case of 1c with Na[BH$_4$] we envisage the formation of up to three possible products. The 1,4-diene product 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 (Davies et al 1978), at the unmethylated site) should enable an endo rearrangement to a 1,3-diene. Formation of this 1,3-diene via the mechanism depicted in scheme 1a would involve an intramolecular nucleophilic addition of hydride from the suggested metal-hydride intermediate to one of the methylated sites of the intermediate cyclohexadienyl ring. Formation of the alternative 1,3-diene complex would occur by direct 1,2-double addition (scheme 1b).

These three possible isomers should be readily distinguished by their $^1$H NMR spectra. The 1,4-diene complex is symmetrical and would therefore give rise to a singlet resonance for the prochiral protons of the cyclophane coordinated deck. The 1,3-diene species are both asymmetric and would cause a splitting of the coordinated ring resonance into an AA'BB' pattern as observed in other chiral [2:2]paracyclophane compounds (Elsegood 1991; Elsegood et al 1992). In practice we find that the reaction of 1c with both red-Al and Na[BH$_4$] gives a yellow solid $[\text{Ru}(\eta^6-C_{16}H_{16})(\eta^6-C_6\text{Me}_3H_3)]$ 2c displaying an AA'BB' coupling pattern for the protons of the coordinated cyclophane ring in its $^1$H NMR spectrum, 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. Also, a resonance observed at $\delta$ 0.44 ppm ($^2J = 13.1$, $^3J = 3.3$ Hz) assigned to the endo hydrogen atom of the diene ring, is not a doublet as would be expected. Instead, this signal is a doublet of doublets displaying coupling constant typical of both geminal and vicinal coupling. The endo hydrogen atom could only be coupled to both exo protons in this way if the formation of 2c results from a direct 1,2-double addition in the same way as in the hexamethylbenzene derived diene, described above, in spite of the availability of an endo hydrogen atom. The $^1$H NMR assignments for 2c were confirmed by preparation of the deuterium analogue and extensive homonuclear decoupling experiments.
Action of Na[BH₄] upon the durene (1,2,3,4,5-tetramethylbenzene) complex 1b in THF over a period of ca. 12 hours results in the formation of a (diene)ruthenium(0) complex [Ru(η⁶-C₆H₁₂)₄(η⁴-C₆Me₄H₄)], 2b. According to arguments based on the accumulation of partial positive charges on the arene carbon atoms (Davies et al 1978; Astruc 1991) 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 a large splitting of the ¹H NMR resonance arising from the protons of the coordinated cyclophane deck. The remainder of the spectrum bears a strong resemblance to that of 2c and selective homonuclear decoupling experiments along with analysis of coupling constants implies that, like 2c, 2b 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.

Reduction of the p-cymene complex 1a with red-Al or Na[BH₄] (in the absence of aqueous quenching) also results in the formation of a chiral 1,3-diene complex of formula [Ru(η⁶-C₁₆H₁₆){η⁴-1-Me-4-(CHMe₂)C₆H₆}], 2a, the product of a direct 1,2-double hydride addition at the least alkylated sites, as would now be expected. The methyl and iso-propyl substituents occupy the two terminal olefinic sites, C(1) & C(4), whilst the two olefinic hydrogen atoms occur as an AB quartet in the ¹H NMR spectrum. Surprisingly, if the reduction is carried out with Na[BH₄] and water added to the reaction mixture a different isomer is obtained, [Ru(η⁶-C₁₆H₁₆){η⁴-2-(CHMe₂)-5-MeC₆H₄}], 2a'. This complex is characterised by the observation of a single olefinic doublet (δ 4.24 ppm) in place of the AB quartet observed for 2a and the appearance of a multiplet corresponding to the terminal olefinic hydrogen atoms on C(1) and C(4). Strong evidence for the aliphatic nature of the methyl substituent on C(5) is the doublet resonance at δ 0.72 ppm (J = 6.7 Hz). In 2a the methyl substituent is attached to the terminal olefinic site C(1) and occurs as a singlet (δ 1.22 ppm). The assignment of the ¹H NMR spectrum of 2a' 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 2a' could result from a net exo [1,3] H-shift of 2a, but not an endo metal-hydride mediated rearrangement.

The observation of 1,2-double additions in complexes 2a–2d 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 (Astruc 1985, 1991). Extended Hückel calculations on the cation [Fe(η⁶-C₆H₆)(η⁴-C₆H₄)]⁺ have demonstrated that the greatest partial positive charges reside on the η²-benzene ring (+ 0.04 – + 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 (Neto and Sweigart 1990). 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 and so 1,4- or 1,3-double additions would be expected (as observed in the red-Al reduction of 1d). The charge at the site ortho to the sp³ carbon atoms is actually negative (– 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 of the reaction is more satisfactory (Astruc 1985, 1991).
Clearly a fine balance exists between the factors affecting regioselectivity in double nucleophilic addition reactions at ruthenium centres. The observation of 1,4-additions at a given ring when red-Al is used as the reducing agent could be a factor 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, osmium (Burrows et al 1980) 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 products.

2.2 Protonation reactions to form agostic complexes

Reaction of the electron-rich ruthenium(0) 1,3-diene complex 2d with H[BF₄] (40% aq) in hexane results in the formation of a pale yellow, air- and moisture-stable precipitate of [Ru(η⁶-C₁₆H₁₆)(C₆Me₆H₃)][BF₄], 3d. The room temperature ¹H NMR spectrum of 3d exhibits three resonances of equal intensity arising from the six methyl substituents of the C₆Me₆H₃ ligand. A further aliphatic resonance was assigned to Hₐₓ and a high field “hydridic” signal was also observed [−10−80 ppm (t of sp, Jₜₛ = 4.1 & 2.5 Hz)]. The peak due to the coordinated deck of the [2,2]paracyclophane ligand occurred as a singlet (implying an apparent plane of symmetry in the C₆Me₆H₃ ligand) at δ 4.80. This is at the higher field end of the chemical shift range expected for a monocationic ruthenium(II) species (Elsegood 1991). The symmetrical nature of the spectrum apparently implies that 3d exists as a metal hydride in its ground state, and contains an η⁶-C₆Me₆H₂ ligand coordinated as a 1,3-diene, consistent with protonation and oxidation of the metal centre [cf. oxidation of the ruthenium(0) bis(phosphine) compounds [Ru(η⁶-C₆Me₆)(PR₃)₂] with [NH₄][PF₆] to give the ruthenium(II) hydrido complexes [Ru(η⁶-C₆Me₆)(PR₃)₂H][PF₆]] (Werner and Werner 1978, 1979, 1982). 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 (Brookhart et al 1988) interaction.

The room temperature ¹H coupled ¹³C spectrum of 3d is also relatively simple, displaying only three resonances for the C₆ ring carbon atoms. The observed ¹JC-H on the resonance at δ 59.25 is only 36 Hz, and that doublet signal collapses to a singlet displaying strong NOE enhancement in intensity with respect to the remainder of the peaks in the spectrum on irradiation of the hydridic proton resonance. These results indicate that the hydridic proton does indeed form part of an agostic CH bond. Although the observed coupling is inconsistent with the formulation of 3d as a full hydride (estimated coupling constant in the region 0−10 Hz²) it is also atypical of an agostic CH bond for which a value of 60−100 Hz would be expected (Brookhart et al 1982, 1988). Therefore the coupling of 36 Hz must be rationalised as a dynamic average (scheme 2) of the two static couplings of the agostic proton with Cᵦ and Cᵦ, i.e. in a slow exchange regime ¹JC-H ≈ 72 and ¹JC-H ≈ 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 coordinated deck of the [2:2] paracyclopheane ligand. In the static complex this resonance would be expected to exhibit an AA'BB' pattern 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 (Bennett and Matheson 1978). Use of a mixed CD2Cl2/CHF2Cl solvent allowed examination of the spectrum down to $-135^\circ$C resulting in the observation of a new set of signals strongly indicative of the loss of the dynamic plane of symmetry in the C6Me6H3 ligand. At this temperature four distinct resonances could be distinguished due to the methyl substituents on C', C', C', and C (δ 2.01, 1.62, 1.49 and 1.06 ppm respectively). The latter peak exhibited doublet coupling as expected in the static structure. Two signals were also observed for the two Hexo protons (δ 1.39 and 0.95 ppm) whilst the remaining two methyl substituents were unresolved. The origins of the exo and agostic protons in 3d were confirmed by a series of deuteration studies.

Interestingly the protonation of the 1,4-diene complex [Ru(η6-C18H18)(η4-3,6-C6Me6H2)] (prepared by red-Al reduction of 1d) with H[BF4] results in the formation of the agostic compound [Ru(η6-C18H18)(η3-(HCH2)(CH2)C6Me4H4)] [BF4] which is an isomer of 3d. Like 3d the 1H NMR spectrum of this complex is deceptively simple at room temperature, the most notable feature of the spectrum being a broad singlet, integrating for five protons, at δ $-1.52$ ppm. Selective decoupling of that signal produces no changes in the remaining resonances in the spectrum. The singlet due to the coordinated 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 $-135^\circ$C suggest that the complex is undergoing two dynamic processes (scheme 3):

(a) Exchange of an agostic proton between the terminal sites Cn/C'n.
(b) Agostic methyl group rotation.

Surprisingly the slower of these dynamic exchanges is process b, agostic methyl rotation. At $-50^\circ$C the 5H resonance at δ $-1.52$ was replaced by two broad signals
at $\delta - 0.90$ (2H) and $-9.92$ (1H) ppm. A further 2H resonance would be expected in the region of $\delta$ ca. 2.5 but was apparently too broad to be observable at this temperature. The resonance at $\delta - 9.92$ ppm occurs at a very similar chemical shift to the agostic signal for $C_b$-H in 3d and by analogy is assigned to the agostic proton $H_a$ whilst the resonance at $\delta - 0.90$ ppm probably corresponds to the syn protons $H_c$ and $H'_c$ (scheme 3). At this temperature the resonance due to the protons of the coordinated deck of the cyclophane ligand remained a sharp singlet implying that the molecule retains a dynamic plane of symmetry. Lowering the temperature to $-80^\circ C$ results in the sharpening of the "hydric" 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 $-50^\circ C$ and $-80^\circ C$ the resonance at $\delta - 0.90$ ppm disappears once more to be replaced by two broad 1H signals $\delta 0.10$ and $-1.85$ ppm whilst the resonances due to $Me_d/Me'_d$ and the endo-protons $H_e/H'_e$ as well as the signal for the coordinated cyclophane deck broaden significantly. At $-100^\circ C$, 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 coordinated deck of the cyclophane ligand into two broad signals. The hydridic resonance at $\delta - 9.92$ ppm now occurs as a triplet due to coupling to only $H_a$ and $H_c$ with a $2J_{H-H} = ca. 14$ Hz, consistent with geminal coupling.

These results contrast sharply with the fluxional processes observed by Bennett et al (1992) in the closely related agostic diphosphine compound $[Ru(\eta^3-(CHCl)(C_6Me_4)\{(Z)-Ph_2PCH=CHPh_2\}(PMMe_2Ph)]PF_6$ and related examples. In these complexes agostic methyl rotation (analogous to process b in scheme 3) is extremely rapid and could not be frozen out at temperatures down to $-90^\circ C$. 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 timescale at temperatures below $+60^\circ C$. These large differences in exchange rates may be rationalised by arguing that the agostic interaction in our compound is much stronger than in the $o$-xylylene-phosphine analogues (Bennett et al 1992) where long range interactions between the uncoordinated, 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 the 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-Ha interaction.

Reaction of the pentamethyl and tetramethyl complexes 2c and 2b with $H[BF_4]$ also results in the formation of agostic protonolysis products $[Ru(\eta^6-C_{16}H_{16})\{(Z)-Ph_2PCH=CHPh_2\}(PMMe_2Ph)]BF_4$ ($n=5, 3c; 4, 3b$). Consistent with the proposed 1,3-diene structures of 2c and 2b, the metal atoms in 3c and 3b are coordinated 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 $3J_{H-H}$ coupling constants. The coordinated deck of the paracyclophe ligands in each compound occurs as an AA'BB' quartet 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 3c these protons occur at similar chemical shifts ($\delta - 4.56$ and $- 5.25$ ppm) and it would seem likely that each spends an approximately equal proportion of their time in agostic coordination to the metal centre. In contrast, one resonance in compound 3b occurs at much higher field than the other ($\delta - 7.68$ $cf. - 1.88$ ppm) 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 3b, 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 $H[BF_4]$ (although the actual origins of the each of the endo hydrogen atoms is likely to be unknowable as a result of rapid scrambling). These results are summarised in scheme 4 which presents the two fluxional processes (processes a and b) responsible for the observed exchange in 3c and 3b. Protonation of 2c and 2b doubtless proceeds initially in a manner analogous to that observed for 2d to give a complex of type I or type II analogous to 3d, 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...
Scheme 4. Fluxionality in the agostic complexes \([\text{Ru}(\eta^6-\text{C}_{16}H_{16})(\eta^3-\text{C}_6\text{Me}_3\text{RH}_a)][\text{BF}_4] \]
\((R = \text{Me} \ _3c, \text{H} \ _3b)\): (a,a') exchange of agostic proton; (b) transfer of agostic interaction.

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 3c molecules of types I/II and types III/IV are present in roughly equimolar amounts. In contrast, for 3b the thermodynamics of the system significantly favour the type III/IV coordination. Extensive variable temperature (+ 50°C to −135°C) \(^1\text{H}\) and \(^{13}\text{C}\) NMR measurements are completely consistent with these propositions as to structures and dynamic behaviour.

3. Conclusions

Incorporation of [2-2]paracyclophane in complexes of the type \([\text{Ru}(\text{arene})(\text{arene}')]\)^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.
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