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Some reactions of $[(\eta^6\text{-}C_6Me_6)Ru(\eta^6\text{-}[2.2]paracyclophane)][BF_4]_2$ with nucleophiles

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Abstract

Single addition of the nucleophiles X^- (X = H, CN, OH) to the less sterically hindered ring in $[(\eta^6\text{-}C_6Me_6)Ru(\eta^6\text{-}C_{16}H_{16})][BF_4]_2$ (1) proceeds smoothly to produce, as the sole product, $[(exo\text{-}\eta^5\text{-}C_6Me_6X)Ru(\eta^6\text{-}C_{16}H_{16})][BF_4]$. Use of $Na[BD_4]$ in place of $Na[BH_4]$ gives the expected shift in $\nu(C\text{–}H_{exo})$ in the infrared spectrum.

Nucleophilic addition to coordinated arenes is of significant interest as a synthetic route to arene functionalisation [1]. While bis(arene)ruthenium complexes are expected [2] to be around thirty times less electrophilic than their iron analogues they display a number of advantages which make them the more attractive alternative in this type of work. These advantages include, (a) the ready availability, via the Bennett [3] and Rybinskaya [4,5] syntheses, of unsymmetrical bis(arene)Ru complexes, and (b) the absence of interfering electron transfer reactions [6,7,8] which can occur on the addition of carbon donor nucleophiles and result in the formation and rapid decomposition of unstable nineteen and twenty electron species. Use of the highly sterically hindered [2.2]paracyclophane ligand has recently been shown to direct nucleophilic attack onto less hindered arenes coordinated to the same metal centre [9], to produce η^4-diene complexes such as $[(\eta^4\text{-}C_6Me_6H_2)Ru(\eta^6\text{-}C_{16}H_{16})]$. In addition, protonation of an η^4-[2.2]paracyclophane compound, $[(\eta^6\text{-}C_6Me_6)Ru(\eta^4\text{-}C_{16}H_{16})]$, gives a coordinated η^5-cyclophane, in $[(\eta^6\text{-}C_6Me_6)Ru(\eta^5\text{-}C_{16}H_{17})]^+$, with the added hydrogen atom in the *endo* position [9]. The reaction is believed to involve the initial formation of a metal hydride followed by proton transfer to the carbocyclic ring. We now report preliminary results of a study involving the use of the paracyclophane ligand to direct *single* nucleophilic attack onto a number of η^6-arenes. The question of *exo* or *endo* addition has been examined by a study of the effects of deuterium isotopic substitution on the solid state infrared spectra of the products.

The starting material $[(\eta^6\text{-}C_6Me_6)Ru(\eta^6\text{-}C_{16}H_{16})][BF_4]_2$ (**1**) was prepared by a published procedure [3,10–12]. Reaction of **1** with sodium borohydride in methanol at room temperature caused an immediate colour change to dark greenish brown.

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Subsequent extraction with dichloromethane and precipitation gave an air-stable, bright yellow product [(*exo*-η^5-C_6Me_6H)Ru(η^6-$C_{16}H_{16}$)][BF_4] (**2**) in ca. 50% yield. This compound is isomeric with that reported by Boekelheide et al. [9]. The ^1H NMR spectrum * of **2** clearly shows the expected quartet due to the incoming hydrogen at 2.00 ppm and a corresponding doublet for the adjacent methyl group (1.01 ppm, ^3J(H–H) 7.0 Hz). The infrared spectrum displays a band at 2813 cm^{-1} corresponding to ν(C–H_{exo}) and microanalytical data supports the proposed formulation. Interestingly **2** is not the product predicted by the rules proposed by Davies et al. [13], which suggest that a charge controlled attack at the less alkylated, i.e. paracyclophane, coordinated ring should occur. This result indicates that for this particular type of compound the nucleophilic addition reactions are sterically rather than electronically controlled. When OH^- and CN^- were used as nucleophiles analogous products were obtained, attack occurring solely at the hexamethylbenzene ring. As expected for a ruthenium compound no problems arising from competing electron transfer decomposition pathways were encountered when the carbon donor CN^- was used [6,7,8].

When sodium borodeuteride, Na[BD_4], was used compounds with a deuteron added to the arene ring were obtained *. Studies of infrared isomer shifts can reveal whether attack has been *exo* or *endo*. The compound [(*exo*-η^5-C_6Me_6D)Ru(η^6-$C_{16}H_{16}$)][BF_4] (**3**) exhibits the expected differences in its infrared spectrum [14] compared with that of **2**. The absence of the band at 2813 cm^{-1} and appearance of a band at 2107 cm^{-1} indicate that nucleophilic addition is *exo*, an observation which is consistent with virtually all previous work on this type of system [13].

Although it might seem surprising that the Na[BH_4] reduction of a dication gives a monocation rather than a neutral compound, there is a well established precedent for such a reaction in areneruthenium(II) chemistry [15], the reaction of Na[BH_4] with [(η^6-$C_6H_3Me_3$)Ru(PMe_2Ph)(1,10-phen)][PF_6]$_2$ being known to give [(η^5-$C_6H_4Me_3$)Ru(PMe_2Ph)(1,10-phen)][PF_6]. In earlier studies [16] of the reduction of various [(η^6-arene)$_2$Ru]$^{2+}$ ions by Na[BH_4] in anhydrous THF indicated that neutral arene-cyclohexadiene complexes were formed exclusively in high yield, but it was noted that the use of H_2O as a solvent led to the formation of small amounts of monocationic arene-cyclohexadienyl-ruthenium products [16]. In the light of this observation it seems likely that the choice of methanol as the solvent for these studies is responsible for the observation of single hydride attack, leading to the formation of the monocationic product.

We are carrying out further studies of nucleophilic addition to the compounds [(η^6-arene)M(η^6-[2.2]paracyclophane)]$^{2+}$, with a view to investigating further the factors governing the site of attack within the arene ring. Attempts are also in progress to observe attack by nucleophiles on the [2.2]paracyclophane ligands of [(η^6-$C_{16}H_{16}$)$_2$Ru]$^{2+}$.

* ^1H NMR data for [(*exo*-η^5-C_6Me_6H)Ru(η^6-$C_{16}H_{16}$)][BF_4] (400 MHz, $CDCl_3$, 298 K): δ 5.04 (s, 4H), 6.81 (s, 4H), 2.86 (m, 4H), 3.23 (m, 4H) ppm, η^6-$C_{16}H_{16}$; δ 1.01 (d, ^3J(H–H) 7.0 Hz, 3H), 1.34 (s, 6H), 1.87 (s, 6H), 2.28 (s, 3H), 2.00 (q, ^3J(H–H) 7.0 Hz, 1H) ppm, η^5-C_6Me_6H.
^1H NMR data for [(*exo*-η^5-C_6Me_6D)Ru(η^6-$C_{16}H_{16}$)][BF_4] (400 MHz, $CDCl_3$, 298 K): δ 5.10 (s, 4H), 6.83 (s, 4H), 2.88 (m, 4H), 3.26 (m, 4H) ppm, η^6-$C_{16}H_{16}$; δ 1.02 (s, 3H), 1.36 (s, 6H), 1.89 (s, 6H), 2.30 (s, 3H) ppm, η^5-C_6Me_6D.

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