JOM 23291PC

Preliminary Communication

Cyclohexenyl [2.2]paracyclophane complexes of ruthenium(II): highly fluxional agostics from the sequential reduction of arenes

Jonathan W. Steed and Derek A. Tocher

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

(Received September 3, 1992)

Abstract

Reduction of the (arene)(paracyclophane)ruthenium(II) complex $[Ru(\eta^6\text{-}C_6Me_6)(\eta^6\text{-}C_{16}H_{16})][BF_4]_2$ (**1b**) with $Na[BH_4]$ gives in contrast to the analogous Red–Al reduction a mixture of ruthenium(0) diene products, chiefly the 1,3-diene complex $[Ru(\eta^4\text{-}1,3\text{-}C_6Me_6H_2)(\eta^6\text{-}C_{16}H_{16})]$ (**2c**). Complex **2c** reacts with aqueous $H[BF_4]$ to generate the agostic species $[Ru(\eta^3\text{-}C_6Me_6H_3)(\eta^6\text{-}C_{16}H_{16})][BF_4]$ (**3**). The complex is highly fluxional with the single *endo* agostic hydrogen atom exchanging rapidly between the two terminal olefinic carbon atoms of the cyclohexadiene unit. The formulation of the complex has been confirmed by the preparation of the di-deutero analogue.

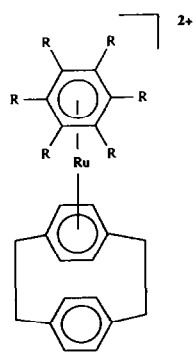
It is well established that the coordination of unsaturated organic fragments to a transition metal centre results in activation of the olefin to nucleophilic attack, and it has been both suggested and experimentally realised that such reactions can form the basis for a viable synthetic method for arene and diene functionalisation [1–4].

Recently we have shown that the polyaromatic arene [2,2]paracyclophane displays only a very limited reactivity towards nucleophiles when coordinated to a metal centre [5,6]. The reactivity and size of paracyclophane make it an effective "blocking agent", exerting steric, as opposed to kinetic [7], control over reaction products. Indeed, even poorly electrophilic arenes such as hexamethylbenzene display a significant reactivity towards nucleophiles when complexed with metal-paracyclophane fragments [5,6]. We have established that single nucleophilic additions may readily occur to the arene ligands in a range of (arene)(paracyclophane) ruthenium(II) complexes under wet aerobic conditions, and have briefly examined the regioselectivities of such reactions.

Paracyclophane also directs double nucleophilic additions of hydride on to other arenes coordinated to the same metal centre; the action of the reducing agent Red–Al on the cations $[Ru(arene)([2.2]paracyclophane)]^{2+}$ (arene = benzene, **1a**; and hexamethylbenzene, **1b**) results in the formation of the ruthenium(0) 1,3-diene compound $[Ru(\eta^4\text{-}C_6H_8)(\eta^6\text{-}C_{16}H_{16})]$ (**2a**) and the 1,4-diene compound $[Ru(\eta^4\text{-}C_6Me_6H_2)(\eta^6\text{-}C_{16}H_{16})]$ (**2b**) [8], respectively. These reactions contrast with those in which double nucleophilic addition to $[Ru(\eta^6\text{-arene})_2]^{2+}$ cations gives bis(cyclohexadienyl)ruthenium(II) species [4,9,10].

Electron-rich ruthenium(0) complexes such as **2a** and **2b** display little further reactivity towards nucleophiles but the metal centre is reactive towards electrophiles. Protonation of the η^4-cyclophane compound $[Ru(\eta^6\text{-}C_6Me_6)(\eta^4\text{-}C_{16}H_{16})]$ with HCl gives a cyclohexadienyl ruthenium(II) complex $[Ru(\eta^6\text{-}C_6Me_6)(\eta^5\text{-}C_{16}H_{17})][HCl_2]$, probably *via* a ruthenium(II) hydride intermediate [8]. Action of HCl on **2a**, however, brings about loss of the diene ligand to form the dichloride dimer $[\{Ru(\eta^6\text{-}C_{16}H_{16})Cl(\mu\text{-}Cl)\}_2]$ [8]. We now report the preliminary results of our investigations into the regioselectivity of double hydride additions to complexes of type **1** and the subsequent reactivities of the resulting diene species towards protonation.

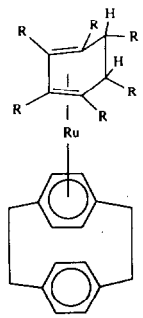
It has previously been shown by Boekelheide *et al.* [8] that reduction of $[Ru(\eta^6\text{-}C_6Me_6)(\eta^6\text{-}C_{16}H_{16})][BF_4]_2$



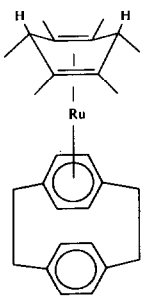
1a R=H
1b R=Me

Correspondence to: Dr. D.A. Tocher.

0022-328X/93/$6.00



2a R=H
2c R=Me



2b

(**1b**) with Red–Al proceeds smoothly to give a high yield of the 1,4-diene complex, **2b**, which has been characterised by X-ray diffraction. We find that using the reducing agent $Na[BH_4]$, over reaction times of *ca.* 24 h a mixture of **2b** and a second product, **2c**, is obtained. Complex **2c** displays an ^1H NMR spectrum ($CDCl_3$) similar in the low field region to that of **2b**, with the singlet resonance for the protons of the coordinated deck of the [2.2]paracyclophane ligand appearing at δ 4.09 ppm, a chemical shift characteristic of a ruthenium(0) complex (*cf.* **2b** 3.95 ppm) [8]. In contrast to **2b**, which displays only two methyl resonances, **2c** exhibits three methyl signals (δ 1.74 (s), 1.10 (s) and 0.56 (d) ppm, all integrating for six protons) as well as the expected quartet resonance (δ 1.18 ppm) for the two *exo* hydrogen atoms. The spectrum of **2c** is consistent with the formation of a 1,3-diene complex, isomeric with **2b**, and generated either by two hydride additions to the hexamethylbenzene ring *ortho* to one another, or by a rearrangement of **2b**. It has been proposed that the 1,3-diene complex **2a**, derived from **1a**, is initially formed as a 1,4-diene but rearranges *via* metal hydride intermediates to give the more thermodynamically stable 1,3-diene product. Such a process requires the availability of *endo* hydrogen atoms on the cyclohexadiene ring, which are clearly absent in the hexamethylbenzene case. Longer reaction times, up to 7 days, do not lead to the formation of **2b**; instead the product consists of **2c** along with small amounts of a third species possibly arising from two nucleophilic additions at *meta* carbon atoms, or alternatively from subsequent slow rearrangements.

Diene complexes of type **2** display little further reactivity towards nucleophiles but the electron rich ruthenium(0) centre is susceptible to attack by electrophiles and we have investigated the reaction of **2c** with $H[BF_4]$. In view of the apparent propensity for isomerisation in this system, reaction conditions were chosen to allow isolation of products as rapidly as possible. To this end aqueous $H[BF_4]$ (40%) was added dropwise with vigorous stirring to a hexane solution of **2c**. Under these conditions a bright yellow precipitate forms at the interface between the aqueous acid and the hexane solution, and after *ca.* 1 h the organic layer is colourless. The yellow precipitate of $[Ru(C_6Me_6H_3)(\eta^6\text{-}C_{16}H_{16})][BF_4]$ (**3**), was isolated by filtration, washed with diethyl ether to remove residual $H[BF_4]$, and subsequently examined by ^1H, $^{13}C\{^1H\}$ and ^{13}C NMR spectroscopy. The presence of the tetrafluoroborate anion was confirmed by infrared spectroscopy.

The ^1H NMR spectrum of **3** * exhibits typical paracyclophane resonances, confirming the retention of that ligand in an unmodified form [11]. The $C_6Me_6H_3$ ligand gives rise to three methyl signals, δ 1.95 (s), 1.38 (d) and 0.72 (d) ppm, each of integral 6H, a doublet of quartets resonance (δ 1.22 ppm) assigned to the two *exo* protons of the C_6 ring, and a high field "hydridic" multiplet, δ −10.80 ppm. Selective homonuclear decoupling experiments demonstrated that this hydridic resonance exhibits significant coupling (i) to the *exo* ring protons and (ii) the methyl resonance at 1.38 ppm. The higher field methyl signal (δ 0.72 ppm) was coupled solely to the *exo* ring protons. This relatively simple spectrum would be consistent with the formulation of **3** as possessing a hydride ground state and a η^4-cyclohexadiene ligand.

In general, however, protonolysis products such as **3** fall somewhere between the two limiting cases of 18 valence electron metal hydrides [such as the cyclopentadienyl iridium complex $[IrH(\eta^5\text{-}C_5H_5)(\eta^4\text{-}C_4H_4Me_2)]^+$ (**4**)] and 16 electron η^3-allylic species. The cobalt and rhodium analogues of **4** display an intermediate, agostic mode of coordination [12]. The existence of significant coupling in **3** between the resonance at δ −10.80 ppm and the methyl and *exo* ring protons of the new ligand ($C_6Me_6H_3$) is not consistent with the formulation of the product as a full hydride, but rather as an agostic species, the agostic interaction taking place at one of the two terminal carbon atoms of the 1,3-diene unit. The relatively simple nature of the room temperature ^1H and ^{13}C (*vide infra*) NMR spectra may be explained in terms of a rapid fluxional

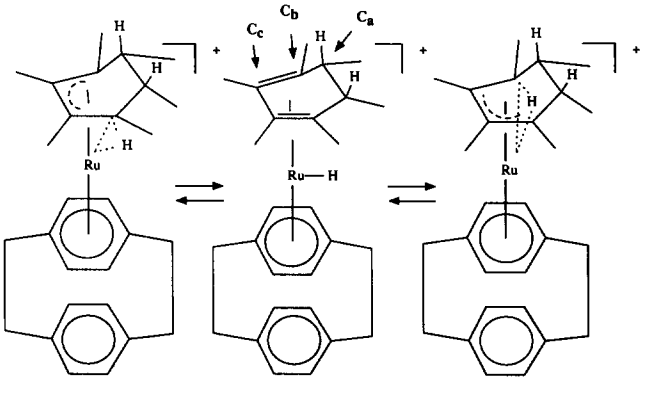
* ^1H NMR data for complex **3** (400 MHz, $CDCl_3$, 293 K): δ 6.85 (s, 4H), 4.80 (s, 4H), 3.25 and 2.98 (AA'XX', 8H), $\eta^6\text{-}C_{16}H_{16}$; 1.95 (s, 6H), 1.38 (d, 6H, J_{obs} (av.) 2.5 Hz), 1.22 (d of q, 2H, J_{obs} (av.) 6.6 and 4.1 Hz), 0.72 (d, J_{obs} (av.) = 6.6 Hz), −10.80 (t of sp, 1H, J_{obs} (av.) 2.5 and 4.1 Hz) ppm, $\eta^3\text{-}C_6Me_6H_3$. ^{13}C NMR (100.6 MHz): δ 139.08 (s), 133.43 (d, J_{obs} (av.) 160.8 Hz), 125.07 (s), 82.18 (d, J_{obs} (av.) 174.6 Hz), 34.22 (t, J_{obs} (av.) 131.2 Hz), 31.35 (t, J_{obs} (av.) 129.9 Hz), $\eta^6\text{-}C_{16}H_{16}$; 91.51 (s, C_c), 59.25 (d, J_{obs} (av.) 36.0 (*ca.* (72+0)/2) Hz, C_b), 38.45 (d, J_{obs} (av.) 129.8 Hz, C_a), 20.43 (q, J_{obs} (av.) 127.6 Hz), 15.47 (q, J_{obs} (av.) 128.0 Hz), 13.20 (q, J_{obs} (av.) 126.8 Hz) ppm, $\eta^3\text{-}C_6Me_6H_3$.

process involving a metal hydride mediated exchange between two equivalent agostic modes shown in Scheme 1. This was partly confirmed by a low temperature ^1H NMR experiment, although a limiting spectrum could not be reached within the accessible temperature range (as observed in related systems [15,16]).

Strong supporting evidence for the agostic nature of **3** comes from its proton-coupled ^{13}C NMR spectrum *, which at room temperature displays three resonances for the ring carbon atoms of the hexamethylbenzene derived ligand (δ 91.51, 59.25 and 38.45 ppm). The former resonance is a singlet while the latter two are doublets. The coupling constant of the doublet resonance at δ 38.45 ppm is 129.8 Hz, consistent with the non-agostic, saturated carbon atoms, C_a (Scheme 1) [13]. The resonance at δ 59.25 ppm displays a smaller separation of only 36.0 Hz, strongly indicative of a reduced C–H bond order, while its chemical shift indicates a partial olefinic character. This smaller separation arises from the dynamic averaging of two carbon environments (^1J(C–H) *ca.* 72 Hz – agostic coupling, and *ca.* 0 Hz – uncoupled). Related unsubstituted cyclohexenyl systems [14,17] containing agostic CH bonds exhibit coupling constants in the range 70–100 Hz.

The assignment of the resonance due to C_b was confirmed by a selective heteronuclear decoupling experiment. Continuous irradiation of the proton resonance at δ −10.80 ppm resulted in the observation of a singlet ^{13}C resonance at δ 59.25 ppm, displaying a strong NOE enhancement relative to the remaining resonances in the ^{13}C spectrum. Hence, we deduce that the terminal olefinic carbon atoms are both coupled to, and relaxing *via*, the agostic proton.

The absence of *exo/endo* hydrogen atom exchange in these complexes was confirmed by the preparation of the di-deutero analogue of **2c**, *viz.* [Ru(η^4-C_6Me_6



3

Scheme 1. Fluxionality in the agostic complex [Ru(η^3-$C_6Me_6H_3$)(η^6-$C_{16}H_{16}$)][BF_4] (**3**).

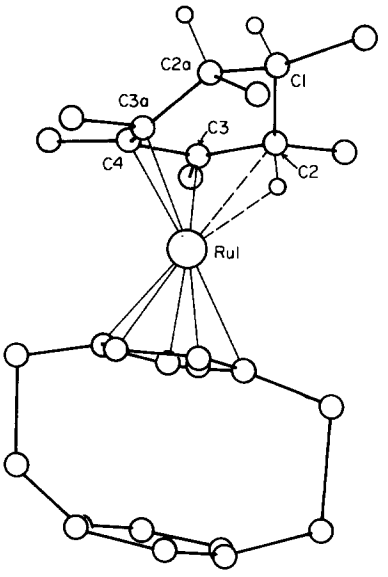


Fig. 1. Structure of the cation [Ru(η^3-$C_6Me_6H_3$)(η^6-$C_{16}H_{16}$)]$^+$ of complex **3** as determined by X-ray diffraction.

D_2)(η^6-$C_{10}H_{16}$)] (**2c′**) (from the action of sodium borodeuteride upon **1b**) and its subsequent protonation to form the agostic complex [Ru(η^3-$C_6Me_6D_2H$)(η^6-$C_{16}H_{16}$)][BF_4] (**3′**). In the ^1H NMR spectra of **2c′** and **3′** the doublet resonances occurring at δ 0.56 and 0.72 ppm respectively in their undeuteriated counterparts, collapsed into broad singlets (^3J(H–D) not resolved) while the multiplet resonance due to the *exo* protons (1.22 ppm) in **3** was absent in **3′**. The $^{13}C\{^1H\}$ spectrum of **3′** showed a 1:1:1 triplet resonance at 37.85 ppm, ^1J(C–D) 20.2 Hz.

The formulation of **3** as being derived from a 1,3- rather than a 1,4-diene was also qualitatively confirmed by a single crystal X-ray structure determination, Fig. 1. Unfortunately the structure is of very limited precision owing to severe disorder of the cyclophane ligand and tetrafluoroborate anion and so quantitative data are not presented. Attempts are in progress to obtain diffraction quality crystals of a sample containing the tetraphenylborate anion.

Detailed work is currently in progress on understanding the regioselectivity of double nucleophilic addition reactions and the isomerism of the resulting ruthenium(0) species. We are also attempting the synthesis of functionalised diene complexes by nucleophilic addition, and the preparation of benzene, *p*-cymene and pentamethylbenzene derived analogues of **3**.

Acknowledgements

We thank the SERC for a studentship (to J.W.S.) and Johnson Matthey plc for generous loans of ruthenium trichloride.

References

1 D. Astruc, *New J. Chem., 16* (1992) 305.
2 M. Uemura, T. Minami, Y. Shinoda, H. Nishimura, M. Shiro and Y. Hayashi, *J. Organomet. Chem., 406* (1991) 371.
3 M. Uemura, H. Nishimura, T. Minami and Y. Hayashi, *J. Am. Chem. Soc., 113* (1991) 5402.
4 C. C. Neto and D. A. Sweigart, *J. Chem. Soc., Chem. Commun.*, (1990) 1703.
5 J. W. Steed and D. A. Tocher, *J. Organomet. Chem., 412* (1991) C37.
6 M. R. J. Elsegood, J. W. Steed and D. A. Tocher, *J. Chem. Soc., Dalton Trans.*, (1992) 1797.
7 S. G. Davies, M. L. H. Green and D. M. P. Mingos, *Tetrahedron, 34* (1978) 3047.
8 R. T. Swann, A. W. Hanson and V. Boekelheide, *J. Am. Chem. Soc., 108* (1986) 3324.
9 D. Jones, L. Pratt and G. Wilkinson, *J. Chem. Soc.*, (1962) 4458.
10 M. I. Rybinskaya, V. S. Kaganovitch and A. R. Kudinov, *J. Organomet. Chem., 235* (1982) 215.
11 M. R. J. Elsegood, *PhD Thesis*, University College London, 1991.
12 Ch. Elschenbroich and A. Salzer, *Organometallics – A Concise Introduction*, VCH, 1989.
13 W. W. Paudler, *Nuclear Magnetic Resonance – General Concepts and Applications*, Wiley, New York, 1987.
14 M. Brookhart, W. Lamanna and M. Beth Humphrey, *J. Am. Chem. Soc., 104* (1982) 2117.
15 M. A. Bennett and T. W. Matheson, *J. Organomet. Chem., 153* (1978) C25.
16 M. Brookhart, M. L. H. Green and R. B. A. Pardy, *J. Chem. Soc., Chem. Commun.*, (1983) 691.
17 M. Brookhart, M. L. H. Green and L.-L. Wong, *Prog. Inorg. Chem., 36* (1988) 1.