

Preliminary communication

Cyclohexadienyl derivatives of (η^6 -arene)(hydrido tris(pyrazolyl) borato) ruthenium(II) compounds

Sameer Bhambri, Derek A. Tocher *

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

Received 22 September 1995

Abstract

The addition of nucleophiles X^- ($X = H, D, OH, CN$) to the complex cation $[Ru(\eta^6-C_6H_6)(Pz_3BH)]^+$ proceeds smoothly to give the neutral cyclohexadienyl compounds $[Ru(\eta^5-C_6H_6X)(Pz_3BH)]$ which are identified by NMR spectroscopy and single crystal X-ray diffraction (for $X = CN$).

Keywords: Ruthenium; Arene; Hydrido; Tris(pyrazolyl)borato; Crystal structure

1. Introduction

Nucleophilic addition to coordinated arenes is of significant interest as a synthetic route to functionalised arenes. Several recent studies have examined this reaction mode for ruthenated arenes [1,2,3]. Single nucleophilic addition to the ' $(\eta^6$ -arene)Ru' fragment gives, in general, stable cyclohexadienyl compounds [2,4–11]. In contrast double nucleophilic addition can result in the formation of a *bis*(cyclohexadienyl)ruthenium(II) compound [1] or a (diene)ruthenium(0) compound [3]. All earlier studies have either been on *bis*(arene) systems or on 'piano stool' complexes, of the type $(\eta^6$ -arene)RuL¹L²L³, where at least one of the ligands L has been a phosphorus donor. In an extension of our earlier studies [2,3] on the reactions of nucleophiles with unsymmetrical *bis*(arene)ruthenium(II) complexes we now report preliminary results on analogous reactions with the cation $[Ru(\eta^6-C_6H_6)(Pz_3BH)]^+$, in which each of the ancillary donor atoms are nitrogen.

2. Results and discussion

Treatment of a suspension of $[Ru(\eta^6-C_6H_6)(Pz_3BH)]PF_6$ in tetrahydrofuran with $Na[BH_4]$ results in the

formation of a yellow solution which, upon evaporation to dryness, yields a slightly air-sensitive yellow solid, in ca. 75% yield. The infrared spectrum of the compound displays a $\nu(CH)$ band at 2782 cm^{-1} , which is the characteristic frequency for the exo C–H bond of an η^5 -cyclohexadienyl ligand. The 1H NMR spectrum displays the expected five sharp signals for the cyclohexadienyl ligand¹. The endo hydrogen gives rise to a complex multiplet (expected doublet of triplets) while the exo hydrogen signal appears as a simple doublet (vicinal coupling to protons on the adjacent carbon is not observed as the dihedral angle between these protons and H_{exo} is close to 90°). This assignment is confirmed when the 1H NMR spectrum of the deuterio derivative, prepared by reaction of $[Ru(\eta^6-C_6H_6)(Pz_3BH)][BF_4]$ with $NapBD_4$, is examined, as the doublet resonance is now absent. This is further confirmed by the infrared spectrum, where the signal at 2782 cm^{-1} is replaced by one at 2088 cm^{-1} in $[Ru(\eta^5-C_6H_6D)]$

¹ 1H NMR data for $[Ru(\eta^5-C_6H_7)(Pz_3BH)]$ (400 MHz, d^6 -acetone, 298 K): hydrido tris(pyrazolyl)borate resonance, δ 5.57 (6H), 6.15 (3H), ca. 4.4 (1H, on boron); cyclohexadienyl resonances, δ 5.67 (t, 1H), 4.55 (dd, 2H), 2.73 (m, $1H_{endo}$), 2.14 (t, 2H), 2.11 (d, $1H_{exo}$). 1H NMR data for $[Ru(\eta^5-C_6H_7)(Pz_3BH)]$ (400 MHz, d^6 -acetone, 210 K): hydrido tris(pyrazolyl)borate resonances, δ 7.78 (1H), 7.46 (2H), 6.45 (1H), 6.07 (2H), 8.83 (1H), 7.53 (2H) ca. 4.4 (1H, on boron); cyclohexadienyl resonances, δ 5.71 (t, 1H), 4.62 (dd, 2H), 2.74 (m, $1H_{endo}$), 2.14 (t, 2H), 2.07 (d, $1H_{exo}$).

* Corresponding author. Email: ucca51t@ucl.ac.uk.

(Pz₃BH)]. A more interesting aspect of the NMR spectrum is the observation that at 298 K the pyrazolyl rings give rise to only two broad resonances (integral ratio 1:2), implying that a fluxional process is operating in solution. This observation has been briefly noted previously [12]. Recording the spectrum of the hydride derivative below 230 K results in the observation of six sharp peaks due to the pyrazolyl protons (the resonances due to the cyclohexadienyl ligand are essentially invariant with temperature). These resonances occur in two well defined subsets (δ 7.78, 6.45, 8.83 ppm and δ 7.46, 6.07, 7.53 ppm integral ratio between sets, 1:2) indicative of two non-equivalent pyrazolyl environments at low temperature. There are several possible explanations which might account for this observation. It is possible that the hydrido\kappa^3 \leftrightarrow \kappa^2 interconversion [13], with perhaps a solvent molecule reversibly entering the ruthenium's coordination sphere. However, we rule out this possibility as, despite repeated attempts, we have been unable to intercept the κ^2 coordinated ligand by reaction of the metal complex with small ligands, such as carbon monoxide. It is more likely that the explanation for our observations (which we have also made in the ¹³C NMR spectra) centres around a process involving restricted rotation about one of the metal-to-ligand axes. In principle either ligand could be involved in such a rearrangement. At the present time we have no definitive evidence for which of the ligands is involved

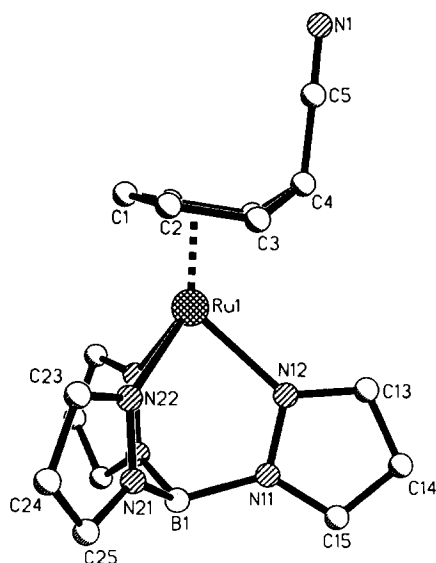


Fig. 1. Molecular structure of $[\text{Ru}(\eta^5\text{-C}_6\text{H}_6\text{CN})(\text{Pz}_3\text{BH})]$ showing the atom numbering scheme. Selected bond lengths (Å) and angles (°): Ru(1)–C(1) 2.149(4), Ru(1)–C(2) 2.128(3), Ru(1)–C(3) 2.165(4) Ru(1)–N(12) 2.124(3) Ru(1)–N(22) 2.139(3), C(1)–C(2) 1.414(4) C(2)–C(3) 1.403(4) C(3)–C(4) 1.502(4), C(4)–C(5) 1.472(6) C(5)–N(1) 1.143(7), N(12)–Ru(1)–N(22) 85.0(1), N(22)–Ru(1)–N(21A) 83.7(1) [atoms labelled 'A' generated by mirror plane through Ru(1), C(1), C(4), C(5), N(1), N(12), N(11) B(1), C(13), C(14) and C(15)].

in this process and we are continuing to pursue this question.

The OH[−] and CN[−] derivatives can be prepared in a similar manner by reaction of $[\text{Ru}(\eta^6\text{-C}_6\text{H}_6)(\text{Pz}_3\text{BH})]\text{PF}_6$ with methanolic NaOH, and a suspension of KCN in tetrahydrofuran, respectively. Each of these compounds exhibits a similar solution behavior to that described above. The compound $[\text{Ru}(\eta^5\text{-C}_6\text{H}_6\text{CN})(\text{Pz}_3\text{BH})]$ is remarkably stable and it has been possible to obtain good quality single crystals, which have been subjected to X-ray crystallographic analysis². The structure (Fig. 1) consists of a κ^3 coordinated hydrido\eta^5-cyclohexadienyl ligand. The molecule is bisected by a crystallographic mirror plane (through atoms Ru(1), B(1) N(12), C(1), and C(4), among others). If one assumes that this is the structure adopted at low temperature in solution then it is immediately apparent that the pyrazolyl ring N(11)–N(12)–C(13)–C(14)–C(15) is unique. The crystallographic study confirms that the incoming nucleophile has added in an exo fashion. Although hydrogen atoms were not located in the structure determination, examination of the angles around C(4) shows clearly that it is sp³ hybridised and hence there is a hydrogen atom endo to the metal. The bond lengths are generally unremarkable. However, it is noticeable that N(12) approaches the metal more closely than does N(22) [Ru–N 2.124(3) and 2.139(3) Å respectively] perhaps as a result of a reduction in the steric interaction between the two ligands as the group C(3)–C(4)C(3A) [atoms labelled 'A' generated by the mirror symmetry] bends back from the plane of the five metalated carbons, C(3)–C(2)–C(1)–C(2A)–C(3A), by some 45.2°, relieving steric congestion.

Extension of this chemistry to compounds containing substituted arenes, and full spectroscopic characterisation of the compounds described herein will appear in the form of a full publication.

² Crystal data for $[\text{Ru}(\eta^5\text{-C}_6\text{H}_6\text{CN})(\text{Pz}_3\text{BH})]$: C₁₆H₁₆BN₇Ru, $M = 418.3$, orthorhombic, space group Pmnb, $a = 10.090(2)$, $b = 13.122(3)$, $c = 13.211(4)$ Å, $V = 1749$ Å³ $Z = 4$, $F(000) = 840$, $D_c = 1.59$ g.cm^{−3}, $\mu(\text{Mo K}\alpha) = 8.9$ cm^{−1}, $\lambda = 0.71073$ Å, crystal dimensions 0.20 × 0.50 × 0.05 mm, $R = 0.0280$, $R_w = 0.0324$. The data were collected on a Nicolet R3mv diffractometer at 293 K in the range $5^\circ \leq 2\theta \leq 50^\circ$. A total of 1778 reflections (1632 unique) were measured, of which 1415 were considered to be observed [$I \geq 3\sigma(I)$]. data were corrected for Lorentz, polarisation and absorption effects. The structure was solved by Patterson methods and developed using alternating cycles of least-squares refinement and difference-Fourier synthesis. The non-hydrogen atoms were refined anisotropically while hydrogens were placed in idealised positions and assigned a fixed isotropic thermal parameter ($U = 0.08$ Å²). Calculations were performed with the SHELXTL PLUS program package on a microVax computer [14]. Atomic coordinates, bonds lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre.

References

- [1] C.C. Neto and D.A. Sweigart, *J. Chem. Soc., Chem. Commun.*, (1990) 1703.
- [2] M.R.J. Elsegood, J.W. Steed, and D.A. Tocher, *J. Chem. Soc., Dalton Trans.*, (1992) 1797.
- [3] J.W. Steed and D.A. Tocher, *J. Chem. Soc., Dalton Trans.*, (1993) 3187.
- [4] H. Le Bozec, D. Touchard, and P.H. Dixneuf, *Adv. Organomet. Chem.*, 29 (1989) 163.
- [5] W. Luginbuhl, P. Zbinden, P.A. Pittet, T. Aembruster, H.B. Burgi, A.E. Merbach, and A. Ludi, *Inorg. Chem.*, 30 (1991) 2350.
- [6] D.R. Robertson and T.A. Stephenson, *J. Organomet. Chem.*, 142 (1977) C31.
- [7] D.R. Robertson, I.W. Robertson, and T.A. Stephenson, *J. Organomet. Chem.*, 202 (1980) 309.
- [8] R. Werner and H. Werner, *J. Organomet. Chem.*, 210 (1981) C11.
- [9] R. Werner and H. Werner, *Chem. Ber.*, 117 (1984) 142.
- [10] R. Werner, H. Werner, and C. Burschka, *Chem. Ber.*, 117 (1984) 152.
- [11] R. Werner and H. Werner, *Chem. Ber.*, 118 (1985) 4543.
- [12] D.J. O'Sullivan and F.J. Lalor, *J. Organomet. Chem.*, 57 (1973) C58.
- [13] U.E. Bucher, A. Currao, R. Nesper, H. Ruegger, L.M. Venanzi, and E. Younger, *Inorg. Chem.*, 34 (1995) 66.
- [14] G.M. Sheldrick, *SHELXL PLUS, an integrated system for refining and displaying crystal structures from diffraction data*, University of Gottingen, Germany, 1986.