Available online at www.sciencedirect.com
SCIENCE DIRECT®
Journal of Organometallic Chemistry 689 (2004) 3108–3112
Journal of Organometallic Chemistry
www.elsevier.com/locate/jorganchem

Note

Synthesis, characterization and molecular structure of the $[(\eta^6\text{-}C_6Me_6)Ru(\mu\text{-}N_3)(N_3)]_2$ complex and its reactions with some monodentate ligands

P. Govindaswamy [a], Hemant P. Yennawar [b], Mohan Rao Kollipara [a,*]

[a] Department of Chemistry, North-Eastern Hill University, Shillong 793 022, India
[b] Department of Biochemistry and Molecular Biology, The Pennsylvania State University, PA 16802, USA

Received 12 April 2004; accepted 7 June 2004
Available online 30 July 2004

Abstract

The reaction of complex $[(\eta^6\text{-}C_6Me_6)Ru(\mu\text{-}Cl)Cl]_2$ (**1**) with sodium azide yielded complexes of the composition $[(\eta^6\text{-}C_6Me_6)Ru(\mu\text{-}N_3)(N_3)]_2$ (**2**) and $[(\eta^6\text{-}C_6Me_6)Ru(\mu\text{-}N_3)(Cl)]_2$ (**3**), depending upon the reaction conditions. Complex **3** with excess of sodium azide in ethanol yielded complex **2**. Complexes **2** and **3** undergo substitution reactions with monodentate ligands such as PPh_3, PMe_2Ph and $AsPh_3$ to yield monomeric complexes. The structure of complex **2** was determined by X-ray crystallography. All these complexes were characterized by micro analytical data and by FT-IR and FT-NMR spectroscopy. Complex **2** crystallizes in the monoclinic space group $P2_1/n$ with $a = 8.5370(11)$ Å, $b = 16.192(2)$ Å, $c = 10.4535(13)$ Å and $\beta = 110.877(2)°$.

Keywords: Hexamethylbenzene; Azide; Ruthenium

1. Introduction

During the last few years, arene–ruthenium(II) complexes have been an area of immense attraction due to their similarity in reactivity with cyclopentadienyl ruthenium(II) half-sandwich complexes. Arene–ruthenium(II) complexes undergo a variety of substitution reactions with various ligands to yield neutral as well as cationic complexes [1]. We had earlier carried out a few reactions of these dimers with Schiff bases and pyrazoles to yield cationic Schiff base compounds and amidine complexes as well as bis disubstituted pyrazole complexes [2]. Recently, a lot of interest has been generated in these complexes due to the synthesis of water-soluble arene–ruthenium complexes, which exhibit antibiotic, antiviral [3] and catalytic activities [4]. The arene–ruthenium(II) complexes having labile chloride groups undergo exchange reactions with bromide and iodide to form bromo and iodo compounds [5]. No reports are available on the reactivity studies of these complexes with azide groups. Recently, the azide complexes have become very important due to the synthesis of triazoles and tetrazoles from these compounds [6]. In continuation of our work, we report here the title compound and its reactions with mono substituted ligands. The molecular structure of the complex **2** is reported as well.

2. Experimental

2.1. General considerations

All solvents were dried and distilled by standard methods. Triphenylphosphine, $PPhMe_2$ and $AsPh_3$ were

* Corresponding author. Tel.: +91-364-272-2620; fax: +91-364-255-0076.
E-mail addresses: mrkollipara@yahoo.com, kmrao@nehu.ac.in (M. Rao Kollipara).

0022-328X/$ - see front matter © 2004 Published by Elsevier B.V.
doi:10.1016/j.jorganchem.2004.06.034

purchased from Merck and used as supplied. The dimer $[(\eta^6\text{-}C_6Me_6)RuCl_2]_2$ (**1**) was prepared by a literature method [7]. Infrared spectra were recorded as KBr pellets using a Perkin–Elmer model 983 spectrophotometer. ^1H and $^{31}P\{^1H\}$ NMR spectra were recorded on a Bruker-ACF-300 (300 MHz) and referenced to tetramethylsilane and H_3PO_4 (85%), respectively, at the Regional Sophisticated Instrumentation Centre (RSIC), NEHU, Shillong, India.

2.2. Synthesis of $[(\eta^6\text{-}C_6Me_6)Ru(\mu\text{-}N_3)(N_3)]_2$ (**2**)

A mixture of $[(\eta^6\text{-}C_6Me_6)RuCl_2]_2$ (100 mg, 0.149 mmol) and excess sodium azide (60 mg, 0.897 mmol) was stirred in dry ethanol (25 ml) for 4 h, whereby the orange-coloured product was separated out. The compound was filtered and washed with diethylether and dried under vacuum (Yield 95 mg, 92%). IR (KBr pellets, cm^{-1}): 2064s (μ-ν_{N3}), 2024s (terminal ν_{N3}).^1H NMR ($CDCl_3$, δ): 2.06 (s, 36H, HMB). Elemental analysis (%) for $C_{24}H_{36}Ru_2N_{12}$: Calc. C, 33.87; H, 5.90; N, 27.43. Found: C, 33.32; H, 6.21; N, 27.33%.

2.3. Synthesis of $[(\eta^6\text{-}C_6Me_6)Ru(\mu\text{-}N_3)(Cl)]_2$ (**3**)

A mixture of complex **1** (100 mg, 0.149 mmol) and twofold sodium azide (18 mg, 0.288 mmol) was stirred in dry acetone (20 ml) for 10 h, whereby the orange-red coloured product was separated out. The compound was filtered and washed with diethylether and dried under vacuum (Yield 87 mg, 85%). IR (KBr pellets, cm^{-1}): 2057s (μ-ν_{N3}). ^1H NMR ($CDCl_3$, δ): 2.09 (s, 36H, HMB). Elemental analysis (%) for $C_{24}H_{36}Ru_2N_6Cl_2$: Calc. C, 42.29; H, 5.32; N, 12.32. Found: C, 42.38; H, 5.09; N, 12.44%.

2.4. Synthesis of complex **2** (second method)

A mixture of complex **3** (100 mg, 0.146 mmol) and excess of sodium azide (38 mg, 0.587 mmol) was stirred in dry ethanol (20 ml) for 2 h, whereby the orange-coloured product was separated out. The compound was filtered and washed with diethylether and dried under vacuum (Yield 86 mg, 84.31%).

2.5. Synthesis of $[(\eta^6\text{-}C_6Me_6)Ru(N_3)_2(L)]$ {L = PPh_3 (**4a**), PMe_2Ph (**4b**) $AsPh_3$ (**4c**)}

A mixture of complex **2** (60 mg, 0.086 mmol) and ligand L (0.173 mmol) was stirred in dry acetone (10 ml) for 12 h, whereby the orange-coloured product was separated out. The compound was filtered and washed with diethylether and dried under vacuum.

Compound **4a** (Yield 45 mg, 42.77%) IR (KBr pellets, cm^{-1}): 2030s (terminal ν_{N3}). ^1H NMR ($CDCl_3$, δ): 1.88 (s, 18H, HMB), 7.41–7.55 (m, 15H, Ph). $^{31}P\{^1H\}$ NMR ($CDCl_3$, δ): 34.66. Elemental analysis (%) for $C_{30}H_{33}RuN_6P$: Calc. C, 59.10; H, 5.45; N, 13.78. Found: C, 59.36; H, 5.14; N, 13.92%.

Compound **4b** (Yield 36 mg, 42.85%) IR (KBr pellets, cm^{-1}): 2037s (terminal ν_{N3}). ^1H NMR ($CDCl_3$, δ): 1.66 (s, 6H, CH_3), 1.89 (s, 18H, HMB), 7.47–7.69 (m, 5H, Ph). $^{31}P\{^1H\}$ NMR ($CDCl_3$, δ): 29.33. Elemental analysis (%) for $C_{20}H_{29}RuN_6P$: Calc. C, 49.43; H, 6.02; N, 17.31. Found: C, 49.36; H, 5.86; N, 17.92%.

Compound **4c** (Yield 45 mg, 40.18%) IR (KBr pellets, cm^{-1}): 2027s. ^1H NMR ($CDCl_3$, δ): 1.86 (s, 18H, HMB), 7.31–7.72 (m, 15H, Ph). Anal. Calc . (%) for $C_{30}H_{33}RuN_6As$: C, 55.13; H, 5.09; N, 12.85. Found: C, 55.28; H, 5.35; N, 12.45%.

2.6. Synthesis of $[(\eta^6\text{-}C_6Me_6)Ru(N_3)(Cl)(L)]$ {L = PPh_3 (**5a**), PMe_2Ph (**5b**), $AsPh_3$ (**5c**)}

These complexes were synthesized using the same procedure given above, except that complex **3** (60 mg, 0.088 mmol) was used as the starting material instead of complex **2**.

Compound **5a** (Yield 41 mg, 38.67%) IR (KBr pellets, cm^{-1}): 2037s (terminal ν_{N3}). ^1H NMR ($CDCl_3$, δ): 1.82 (s, 18H, HMB), 6.94–7.56 (m, 15H, Ph). $^{31}P\{^1H\}$ NMR ($CDCl_3$, δ): 33.68. Elemental analysis (%) for $C_{30}H_{33}RuN_3ClP$: Calc. C, 59.74; H, 5.51; N, 6.96. Found: C, 59.39; H, 5.87; N, 7.06%.

Compound **5b** (Yield 37 mg, 44.04%) IR (KBr pellets, cm^{-1}): 2037s (terminal ν_{N3}). ^1H NMR ($CDCl_3$, δ): 1.54 (s, 6H, CH_3), 1.76 (s, 18H, HMB), 7.43–7.51 (m, 5H, Ph). $^{31}P\{^1H\}$ NMR ($CDCl_3$, δ): 30.43. Elemental analysis (%) for $C_{20}H_{29}RuN_3ClP$: Calc. C, 50.15; H, 6.10; N, 8.77. Found: C, 49.12; H, 5.86; N, 8.43%.

Compound **5c** (Yield 46 mg, 41.07%) IR (KBr pellets, cm^{-1}): 2037s (terminal ν_{N3}). ^1H NMR ($CDCl_3$, δ): 1.78 (s, 18H, HMB), 6.91–7.65 (m, 15H, Ph). Elemental analysis (%) for $C_{30}H_{33}RuN_3ClAs$: Calc. C, 55.68; H, 5.14; N, 6.49. Found: C, 55.37; H, 4.97; N, 6.62%.

3. X-ray crystallography

Diffusing hexane into dichloromethane solution of complex **2** grew suitable crystals. A suitable crystal of complex **2** was mounted on a Bruker SMART APEX CCD area detector system equipped with a graphite monochromator and a Mo Kα fine-focus sealed tube (λ = 0.71071 Å) with ψ range 0–200° at increment of 1.0–2.3° and $D_{max} - D_{min}$ = 12.45–0.81 Å. The structure was solved by direct methods using the program SHELXS-97 [8]. The refinement and all further calculations were carried out using SHELXL-97 [9]. The hydrogen atoms have been included in calculated positions and

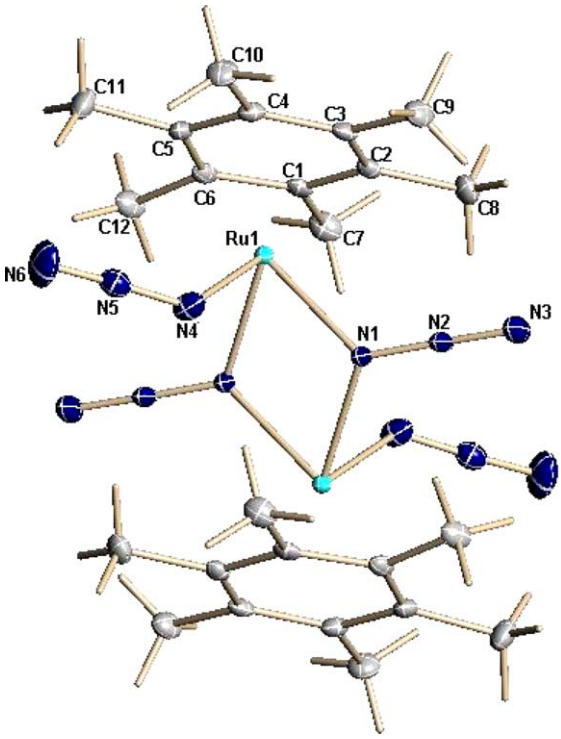
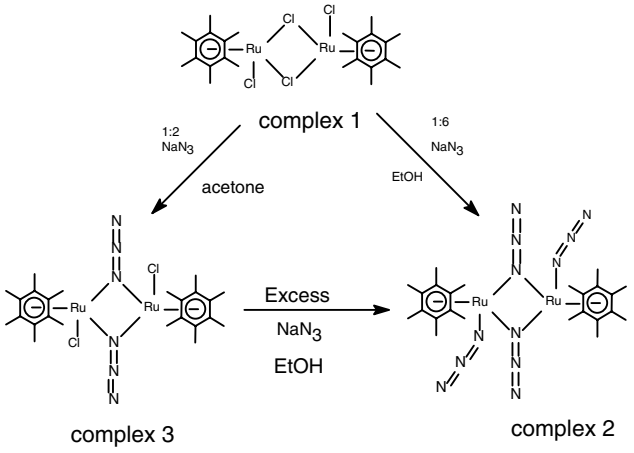


Fig. 1. ORTEP diagram of the complex **2** with 50% probability thermal ellipsoids.

treated as per the 'riding' model, using the SHELXL default parameters. All non-H atoms were refined anisotropically, using a weighted full matrix least-squares fit on F^2. An ORTEP [10,11] diagram of the molecule is presented in Fig. 1.

4. Results and discussion

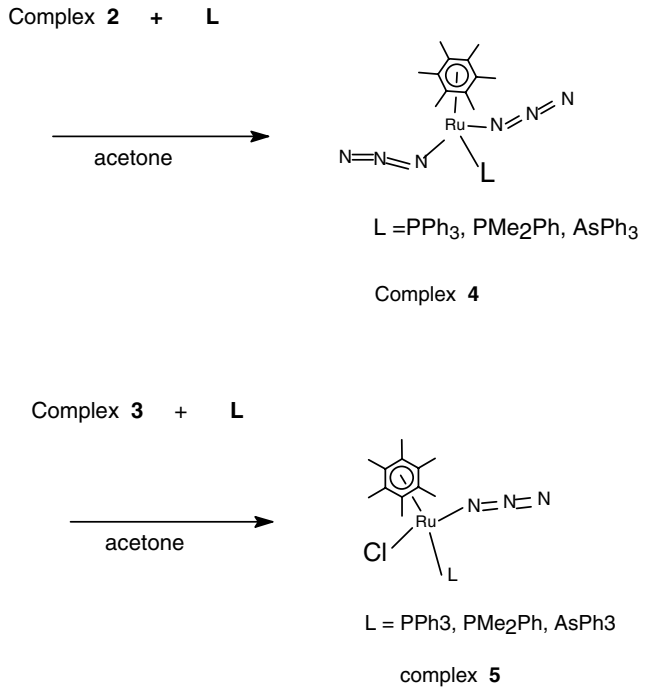
The chloro arene–ruthenium dimer **1**, which reacted with excess of sodium azide in ethanol gave the orange-coloured tetra-azido complex **2** in 92% yield. When the reaction was carried out with the complex **1** and sodium azide in 1:2 molar ratio in acetone, the orange-red di-azido complex **3** was obtained in 85% yield. The similar reaction in the case of *p*-cymene dimer $[(\eta^6\text{-}C_{10}H_{14})Ru(\mu\text{-}Cl)Cl]_2$ invariably yielded only bridged disubstituted azido complex $[(\eta^6\text{-}C_{10}H_{14})\text{-}Ru(\mu\text{-}N_3)Cl]_2$ analogous to complex **3** [12a]. The complex **3** with excess of sodium azide gave the complex **2**. These complexes are stable in air and soluble in polar solvents such as chloroform and dichloromethane, but insoluble in non-polar solvents such as hexane and pentane. The infrared spectrum of complex **2** shows two characteristic bands – one in the region of terminal azide ligands at 2024 $cm^{-1}$and another in the region of bridging azide ligands at 2064 cm^{-1} [13]. Complex **3** exhibits the characteristic band for the bridging azide groups at 2057 cm^{-1}, indicating that no terminal azide ligands are present. This was further confirmed by the elemental analysis, which indicated only two azide groups.



The proton NMR spectrum of the complex **2** exhibits a strong peak at 2.06 ppm for the hexamethylbenzene protons, whereas in the case of complex **3** the signal is observed at 2.09 ppm. The molecular structure of complex **2** was determined by X-ray crystallography (Fig. 1). Complex **2** crystallizes in the monoclinic space group *P*2(1)/*n* with centro-symmetry. The geometry around the ruthenium atom in the complex **2** is octahedral, where the hexamethylbenzene occupies three coordination positions. The compound has a piano stool type structure, where the bond angle N(1)–Ru(1)–N(4) around ruthenium is equal to 81.55(7)°, a little lower than for other reported compounds. The bond distance between the centroid of HMB and Ru is 1.663 Å, while the Ru–N bond distances are 2.1520(18) Å for the Ru(1)–N(1) bond and 2.1090(18) Å for the Ru(1)–N(4) bond, which are within the limits of reported complexes [14]. The terminal azide nitrogens have N–N bond distances of 1.188(3) Å for the (N4)–(N5) bond and 1.159(3) Å for the (N5)–(N6). N–N bond distances in the bridging azide nitrogens are 1.209(2) Å for the (N1)–(N2) bond and 1.144(3) Å for the (N2)–(N3) bond. In the case of terminal azide, the N(4)–N(5) bond distance is slightly smaller than the bridging azide N(1)–N(2), whereas N(5)–N(6) distance of terminal azide is slightly longer than the bridging azide N(2)–N(3) distances. However, these bond distances of the bridging and terminal azide nitrogens are close to other reported values [12].

These dimers undergo bridge cleavage reactions with a twofold excess of L [L = PPh_3, PMe_2Ph, $AsPh_3$ (**4**,**5**)] in

acetone, giving the mononuclear complexes **4a**, **4b**, **4c**, **5a**, **5b** and **5c**.



The infrared spectra of these complexes show a strong band in the range of 2037–2026 cm^{-1} due to the terminal azide group [15] along with strong bands due to the phenyl groups of the phosphine ligands. The ^{1}H NMR spectra of these complexes exhibit a strong peak for hexamethylbenzene at 1.88 ppm for complex **4a**, 1.89 ppm for complex **4b** and 1.86 ppm for complex **4c** [16], respectively. The aromatic protons of the ligands **L** appear as multiplets at around 6.91–7.69 ppm for these complexes. The $^{31}P\{^{1}H\}$ NMR spectra of these complexes exhibit a singlet at around 29.33–34.66 ppm for the terminal phosphine group. The ^{1}H NMR spectra of the complexes **5a**–**c** also exhibit strong signals for hexamethylbenzene protons in the range of 1.76–1.89 ppm and multiplets in the range of 7.0–7.7 ppm for the phenyl groups of the phosphine ligands. The methyl group protons of PMe_2Ph appear around 1.66 ppm in the case of complex **4b** and around 1.54 ppm in the case of complex **5b**.

5. Conclusions

It is thus interesting to note that there is a difference in reactivity between the *p*-cymene dimer $[(\eta^6\text{-}p\text{-cymene})Ru(\mu\text{-}Cl)Cl]_2$ and the hexamethylbenzene dimer $[(\eta^6\text{-}C_6Me_6)Ru(\mu\text{-}Cl)Cl]_2$ towards azides and pyrazoles [2c]. The former gives only the disubstituted *p*-cymene ruthenium μ-azido dimer $[(\eta^6\text{-}C_{10}H_{14})Ru(\mu\text{-}N_3)Cl]_2$ irrespective of sodium azide concentration [12a], whereas the latter gives both disubstituted μ-azido and tetrazido substituted complexes. These complexes can undergo a variety of substitution reactions with monodentate and bidentate ligands to yield monomeric compounds as well as bridged dimeric compounds. This work is currently under progress.

Acknowledgement

H.P.Y. acknowledges NSF grant CHE-0131112 for the purchase of the diffractometer.

Appendix A. Supplementary material

Crystallographic data for the structural analysis have been deposited at the Cambridge Crystallographic Data Centre (CCDC), CCDC No. 235560 for complex **2**. Copies of this information may be obtained free of charge from the director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www:http://www.ccdc.cam.ac.uk). Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2004.06.034.

References

[1] V. Cadierno, P. Crochet, J Garcia-Alvarz, S.E. Garcia-Garrido, J. Gimeno, J. Organomet. Chem. 663 (2003) 32.
[2] (a) R. Lalrempuia, M.R. Kollipara, P.J. Carroll, Polyhedron 22 (2003) 605;
(b) M.R. Kollipara, P. Sarkhel, S. Chakraborty, R. Lalrempuia, J. Coord. Chem. 56 (2003) 1085;
(c) P. Govindaswamy, Y.A. Mozharivskyj, M.R. Kollipara (J. Organomet. Chem.).
[3] C.S. Allardyce, P.J. Dyson, D.J. Ellis, P.A. Salter, R. Scopelliti, J. Organomet. Chem. 668 (2003) 35.
[4] H. Harvath, G. Laurency, A. Katho, J. Organomet. Chem 689 (2004) 1036.
[5] M.A. Bennett, A.K. Smith, J. Chem. Soc., Dalton Trans. (1974) 233.
[6] Chao-Wan Chang, Gene-Hsiang Lee, Organometallics 22 (2003) 3107.
[7] M.A. Bennett, T.N. Huang, T.W. Matheson, A.K. Smith, Inorg. Synth. 21 (1982) 74.
[8] G.M. Sheldrick, Acta Cryst. A 46 (1990) 467.
[9] G.M. Sheldrick, SHELXL-97, University of Gottingen, Gottingen, Germany, 1999.
[10] L.J. Farrugia, J. Appl. Cryst. 30 (1997) 565.
[11] XRD Single Crystal Software; Bruker Analytical X-ray Systems: Madison, USA, 2002.
[12] (a) R.S. Bates, M.J. Begley, A.H. Wright, Polyhedron 9 (1990) 1113;

(b) W. Rigby, P.M. Bailey, J.A. McCleverty, P.M. Maitlis, J. Chem. Soc., Dalton Trans. (1979) 371.
[13] P. Paul, K. Nag, Inorg. Chem. 26 (1987) 2969.
[14] T.J. Geldbach, D. Drago, P.S. Pregosin, J. Organomet. Chem. 643–644 (2002) 214.
[15] P. Paul, S. Chakladar, N. Nag, Inorg. Chim. Acta 170 (1990) 27.
[16] (a) R.Y.C. Shin, M.A. Bennett, L.Y. Goh, W. Chen, D.C.R. Hockless, W.K. Leong, K. Mashima, A.C. Willis, Inorg. Chem. 42 (2003) 96;
(b) X.L. Lu, J.J. Vittal, E.R.T. Tiekink, G.K. Tan, S.L. Kuan, L.Y. Goh, T.S.A. Hor, J. Organomet. Chem. 689 (2004) 1978.